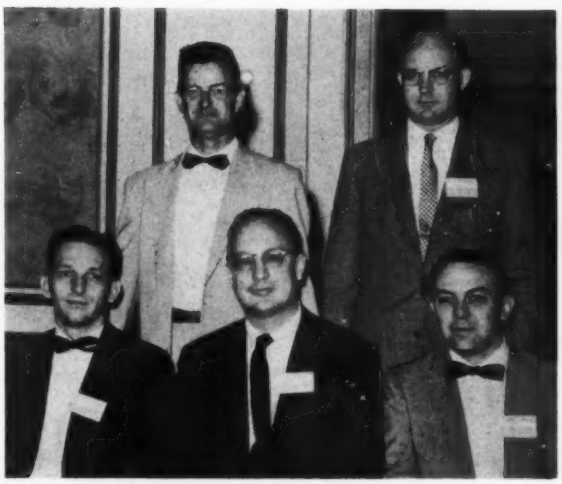
THE GLASS INDUSTRY
THE JOURNAL OF GLASS MANUFACTURING

Glass Division Papers of American Ceramic Society

● THERE WERE 2501 PEOPLE registered at the 61st Annual Meeting of the American Ceramic Society which was held in the Palmer House, Chicago, from May 17 to 21. Visitors came from Europe, Mexico, Canada, and other countries.

The section devoted to glass technology offered 20 papers and featured a symposium on *Behavior of Glass in the Viscoelastic Range*. The committee responsible for this very interesting program was chairmaned by Ralph K. Day of Maumee, Ohio, with the assistance of Robert D. Maurer, Corning Class Works, and Clarence L. Babcock, Owens-Illinois Glass Company.



New Glass Division officers, left to right (standing): Fay V. Tooley, University of Illinois, and Neill M. Brandt, Mellon Institute; (seated) Guy E. Rindone, Department of Ceramic Technology, Pennsylvania State University; August C. Siefert, Owens-Corning Fiberglas Corp.; and Frank R. Bacon, Owens-Illinois Technical Center.

Monday Afternoon

The Monday afternoon sessions were guided by Clarence Babcock because Chairman Ralph Day could not be there.

EVALUATION OF SEVERAL NEW INFRARED TRANSMISSIVE GLASS SYSTEMS, by Francis C. Lin, Westinghouse Electric Corporation, Ceramics Section, Pittsburgh 8, Pennsylvania.

Materials such as oxide glasses, non-oxide glasses, synthetic crystals, and polycrystalline substances, transparent to infrared, were briefly reviewed for their suitability as protective windows in the infrared detection system.

A variety of new non-silicate glass compositions using the oxides of antimony, bismuth, arsenic, tellurium, and geranium as glass formers and Al_2O_3, PbO, MoO_3, WO_3, TiO_2, V_2O_5, LiO_5, Na_2O, and K_2O, as stabilizing oxides were evaluated. Several of their physical properties, such as density, chemical durability, electrical resistivity, linear thermal expansion, melting range, and deformation temperature were also measured.

These glasses in practical thickness of 2.0 mm. transmit 45 to 70 per cent of the incident radiation between 2.5 to 7.0 microns wave-length. All glasses studied had a

New officers and trustees of American Ceramic Society, left to right (seated) George Spencer-Strong, Pemco Corp., president-elect; Oscar G. Burch, Owens-Illinois, president; and Andrew Pereny, Pereny Equipment Co., treasurer. Standing: Albert H. Couch, Libbey-Owens-Ford Glass Co., trustee; James I. Mueller, University of Washington, vice president; John H. Koenig, Rutgers University, vice president; J. J. Canfield, Armco Steel Corp., vice president; Joseph A. Pask, University of California, trustee; and C. J. Koenig, Ohio State University, trustee.

range of deformation temperatures from 400 to 600°C., a variety of thermal expansions, and high electrical resistivity even at temperatures near their deformation points. All glasses except the TeO_2 - Ta_2O_5 glass system have rather poor chemical durability in diluted acid solution.

A concept of the atomic bonding within the glass structure as related to infrared transmission and infrared absorption was presented and discussed. The strong absorption shown in the infrared data was probably caused by atomic or molecular oscillation and, therefore, limited the region of transmission. The absorption of radiant energy within this region owing to the oscillation of free electrons was the major factor which determines the amount of infrared transmission.

RELATIVE ACIDITIES OF GLASSES CONTAINING Al_2O_3 AND TiO_2 AS DETERMINED BY THE OXYGEN ELECTRODE, by D. E. Day, Department of Ceramic Technology, The Pennsylvania State University, University Park, Pennsylvania.

The oxygen electrode described by Tashiro and Forland has been utilized to determine the relative acidities of sodium and potassium silicate glasses containing alumina and titania. The measurements indicate that the replacement of alkali by small amounts of alumina or titania produced glasses of approximately the same relative acidity; however, these glasses were considerably more acid than a similar glass containing equivalent amounts of titania. The converse was true for the sodium silicate glasses. The assumption that the acidity of the glasses is not changed by the traces of silver introduced by the electrodes has been verified by reproduction of the data using platinum as the electrode material.

FURTHER STUDIES OF THE NUCLEATION OF A LITHIUM SILICATE GLASS, by Guy W. Rindone, Department of Ceramic Technology, the Pennsylvania State University, University Park, Pennsylvania.

The importance of platinum nucleation of glass was reviewed. It was pointed out that the optimum condition of crystallization is reached when the platinum particles are extremely small. The effect may be similar to that occurring when metals crystallize.

It had been previously reported by the writer that the presence of platinum nuclei will greatly enhance the rate of crystallization of a lithium silicate glass heated at a constant temperature. Further studies by X-ray diffraction analysis and electron microscopy have been carried out. It has been found that the amount of crystallization which occurs at a given time and temperature reaches a maximum of about 0.005 per cent platinum when the heating time is short. With increasing temperature or time of heat treatment, the amount of crystallization becomes greater as the platinum concentration is increased to 0.025 per cent, the maximum amount introduced. Electron microscopy revealed that prior to any heat treatment, the lithium silicate glass contained a fine structure, even without platinum nuclei.

SUB-SOLIDUS NUCLEATION IN THE SYSTEM Li_2O-Al_2O_3-SiO_2, by Rustum Roy and C. Ruiz-Menacho, Pennsylvania State University, University Park, Pennsylvania.

The paper was presented by Rustum Roy.

"X-Ray Amorphous" mixtures of various types of gels and glasses with compositions in the system eucryptite-silicia-lithium metasilicate have been crystallized under both dry and hydrothermal conditions for varying periods at temperatures between 200° and 900°C.

Because it is the simplest, lithium metasilicate structure is the first to come out of solution. Glass crystallized first in an anhydrous phase and then progressed to a hydrated structure. In the presence of water, glass nucleated much more rapidly than a gel.

CRYSTALLIZATION OF SODIUM DISILICATE GLASS, by Joseph A. Pask, Ceramics Laboratories, Department of Mineral Technology, University of California, Berkeley, California.

Nucleation and growth of sodium disilicate crystals ($Na_2Si_2O_5$) from a glass of the same composition were observed using a high-temperature microscope (the microscope apparatus was described in principle). A high-temperature nucleation from the glass-platinum interface occurred from 450°C. to the melting point of 870°C. and was maximum at 550°C. Low-temperature nucleation occurred at the glass-air interface and was caused by hydration reaction with moisture in the air.

Linear growth rates of crystals as a function of temperature were determined and were compared with published data and calculated values.

Crystallization of glasses is of interest from both a practical and a theoretical point of view. How can one induce or prevent crystallization, and what factors contribute crystallization characteristics?

This investigation was undertaken to study the crystallization of a relatively simple glass which had a straight-forward crystallization path, i. e., the direct freezing of crystals with the same composition as the glass.

The kinetics of crystallization process consist of two parts.

1. Nucleation rate, or rate of appearance of regions of a new phase.
2. Growth rate, or rate of growth of the new regions.

Tammann was the first to study the crystallization of super-cooled liquids.

It was concluded:

1) Crystal growth rates were very sensitive to impurity content.

2) In the region where viscosity is rate controlling, the growth rate represented a maximum determined by the viscosity rather than the polymorphic modification.

3) A polymorphic form will continue to grow far outside its stability range if it is stable with respect to the liquid and if the transformation to the stable form is slow.

4) Heterogeneous nucleation was the only process operating in this glass. Crystals were nucleated at the Pt heating element, or by a hydration reaction.

5) The crystals resulting from the short-term hydration nucleation were all alpha if grown in the alpha stability region or alpha-beta if grown in the beta stability range.

6) Heavily weathered samples, with definite hydrated sodium carbonate coatings on the surface formed beta when heated to 800°C. or F.

Thus, the particular crystal form produced depended both upon the temperature of growth and the nucleation catalyst on which it was grown.

INTERNAL FRICTION OF SIMPLE GLASSES CONTAINING ALKALINE EARTH OXIDE ADDITIONS, by **R. J. Ryder,** Department of Ceramic Technology, the Pennsylvania State University, University Park, Pennsylvania.

Systematic additions of alkaline earth oxides to alkali silicate glasses were found to produce several interesting changes in internal friction plotted as a function of temperature. The two peaks, previously reported by other investigators as appearing in alkali silicate glasses were found to be shifted gradually to higher temperatures, approximately 300°C. This gradual shifting was related to the alkaline earth oxide additions. In some alkali-free silicate and phosphate glasses studied, peaks have been discovered which closely resemble those found in alkali-containing glasses. The results were interpreted on the basis of the influence of the alkaline earth oxides on glass structure.

The effects of the alkaline earth oxide substitution on the durability of the various glasses were discussed and it was pointed out that the considerable differences occurred depending upon the alkali present, i. e. lithium, sodium or potassium.

APPLICATION OF FAR-INFRA-RED SPECTROSCOPY TO THE ASSIGNATION OF STRUCTURAL FORMULAE IN COMPLEX SILICATES, by **V. Stubican and Rustum Roy,** Pennsylvania State University, University Park, Pennsylvania.

This paper was not presented because Mr. Stubican was not present. The abstract, which appeared in the program, follows.

"In an investigation of earlier work which demonstrated the usefulness of infrared spectroscopy in empirical determinations of coordination of cations in simple structures, a study had been made of infrared spectra of synthetic layer lattices of silicates by controlled synthesis. At high temperature and high water pressure it has been possible to vary single ions in a given structure and to determine the main absorption bands associated with any metal-ion oxygen linkage. The following structures have been studied: kaolinite, septichlorite, 10a° beidellites, and sapronites; pyrophyllite and talc; muscovite and phlogapite; 14a° chlorite."

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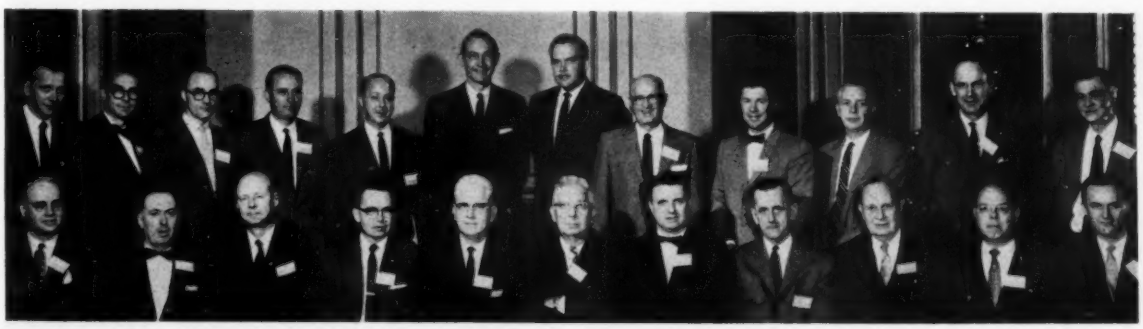


Newly elected Fellows of Society, left to right (seated): Lowell H. Milligan, Norton Co.; Norman H. Stolte, Harshaw Chemical Co.; Edward S. Campbell, Northwestern Glass Co.; Edwin M. Dietterle, Ferro Corp.; Albert R. Lesar, A. P. Green Fire Brick Co.; Ralph E. Grim, University of Illinois; Grant E. Miller, Ferro Corp.; Adrian G. Allison, Battelle Memorial Institute; Walter S. Mayer, Mayer China Co.; Arthur J. Blume, Murray Tile Co.; Edward J. Smoke, Rutgers, State University School of Ceramics (N. J.). Standing: Joseph H. Nandwerk, Argonne National Laboratory; E. Joseph Weiss, University of Texas; J. R. Hensler, Bausch & Lomb Optical Co.; Elburt F. Osborn, Pennsylvania State University; Frederick R. Matson, Pennsylvania State University; Bernard F. Gentsch, United Clay Mines Corp.; Louis R. McCreight, General Electric Co.; Charles S. Cruikshand, Great Lakes Foundry Sand Co.; Donald V. Van Gordon, Metal & Thermit Corp.; Baird L. Dorsey, Jones & Laughlin Steel Co.; and Charles A. Bradley, Jr., and Errol B. Shand, both of Corning Glass Works. J. K. Teague, Jr., Owens-Illinois Technical Center, also a Fellow, does not appear in picture.

Earl A. Garber, left, in whose honor the Research Center is named, discusses metal-encased furnace roof brick with Raymond E. Birch, director of research, and J. Spotts McDowell and W. F. Rochow, research counsellors.

The Garber Research Center

• CONTROLLED EXPANSION, heat-exchange properties, corrosion resistance, high melting points, thermal shock—these are a few of the refractory properties under constant study at the new Garber Research Center of Harbison-Walker Refractories Company, formally opened early last month, in Pittsburgh, Pa.

Dramatic proof of the company's versatile nature is offered by a single plaque set in the silica-brick walk approaching the Center which proclaims that America's first satellite (Explorer I) was launched at Cape Canaveral, Fla., from a pad fashioned from Harbison-Walker's refractory castable. This progressive, forward-looking attitude is easily apparent in the thoroughness of the $2-million Garber Research Center and explains why the company is one of the largest refractory manufacturers in the world.

The Center itself is divided into two main buildings; offices and instrumental research are lodged in one half, and a product development pilot plant, in the other.

In the first building is the laboratory for minerals study where researchers scrutinize the changes which have taken place in refractories while in service—changes in mineralogic content caused by the penetration of furnace fumes, slag and other impurities.

These studies are carried out by means of petrographic equipment such as the emission spectrograph (minor constituents) and x-ray spectrograph (major constituents) for semi-quantitative analysis, and the x-ray diffractometer for identifying crystals and minerals. Also in this section is a well-equipped analytical chemistry laboratory and complete photographic equipment.

In the pilot plant building Harbison-Walker has a complete line of crushing and grinding, screening and mixing equipment for use in the different techniques of pressing, extruding, ramming, gunning and casting.

The kiln area has an electric furnace room and a gas-fired furnace area where studies are made on high-temperature strength and load-bearing capabilities of refractories.

In the gas-fired kiln area there are many reheat or test kilns, some capable of reaching temperatures as high as 3500°F., far greater than that attained in most industrial installations. Throughout this area automation is the guide, assuring that all research testing is under complete control, such as in the ASTM tests for panel spalling and load capabilities.

The pilot plant area contains specialized product development laboratories, like the one designed specifically for the development of castable and monolith refractories; another, for refractory mortars; a third, for small-scale studies or bench scale operations.

For carrying out routine physical refractory tests, there are special facilities adjoining the pilot plant location. Here, studies can be made on transverse strength, abrasion resistance, compression testing, density, apparent porosity, bulk specific gravity, and rate of permeability of furnace gases.

Harbison-Walker has contributed a great deal to the knowledge of refractories and ways in which to improve manufacturing processes involving high temperatures. In glass making, for example, the company has engaged in considerable research dealing with the glass tank crown and methods of applying to it high-temperature silica insulation. This insulation, by greatly reducing the temperature gradient through the crown thickness, prevents the condensation of damaging alkalies which volati-

efractory samples are tested by soaking in contaminating chemicals nd then exposing to cyclic temperature and atmosphere changes.

ize from the batch. Other important glass research rojects of the company include the newer method of orming zircon paving brick by "impact" pressing (re-ults in better density and greater resistance to molten lass, longer life); discovery and investigation of the "oxiduction" effect in glass tank checker chambers be-ause of changes in the chemistry of the atmosphere; nd new refractories for glass manufacture, with a shift oward basic refractories.

Men responsible for leading this research activity include E. T. Hile, vice president; Raymond E. Birch, director of research; Donald F. Stock, laboratory manager; Edwin Ruh, assistant director of research; and Donald F. King, assistant laboratory manager.

Mr. Stock and Dr. Ruh head the management group in the Garber Research Center, the latter having direct supervision over instrumental research. Mr. King is in charge of sales service projects.

Engineers and scientists with various backgrounds make up the technical staff, although there is a predominance of ceramic engineers.

Because Harbison-Walker technical interests are so highly diversified, the company has found it essential to divisionalize its work. One research staff group concerns itself solely with basic refractories (chrome ore, dead burned magnesite, dolomite and olivine); other groups deal with refractories based on such materials as silica, fireclays, bauxite, pure aluminum oxide, zircon, and silicon carbide.

Harbison-Walker produces some 90 per cent of all raw-

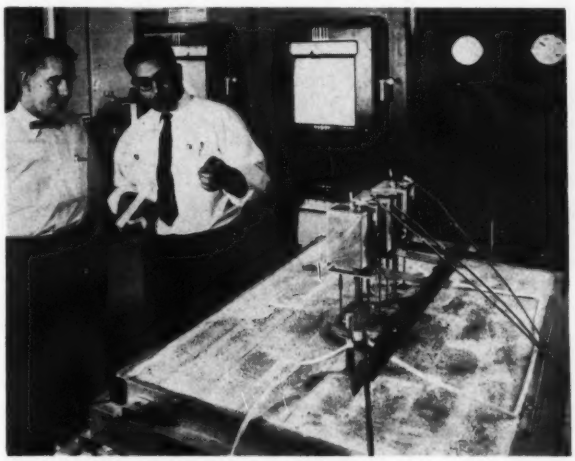
B. C. Ruprecht, chief chemist, working with flame photometer. He devised method for determining alkali content of refractory materials.

material needs; it has mineral reserves in 17 states and operates 60 quarries and mines. Raw materials which the company must purchase include bauxite, alumina, chrome ore and zircon.

Wholly or partially owned subsidiaries are the Northwest Magnesite Company of Cape May, N.J. (dead burned magnesite); Canadian Refractories Ltd.; Marelan, Quebec (basic and high alumina refractories); Clayburn-Harbison Ltd., British Columbia (refractories, face brick and sewer pipe); Harbison-Walker—FLIR, Monterrey, Mexico (various refractories); and Refractories Peruanos S.A., Peru (complete line of refractories).

Earl A. Garber, after whom the Research Center is named, first became associated with Harbison-Walker in 1915 and has been with the company ever since, except for two years (1917 and 1918) in the U. S. Navy.

He returned to the company's Old Harwalk, Ohio, Works in 1918 as shipper, later serving in supervisory capacities at Harbison-Walker's Sciotoville and Portsmouth, Ohio, plants and at its Olive Hill, Kentucky, plant



Don Stock, laboratory manager, and Ray Bier, research physicist, reviewing operation of thermal expansion equipment at Harbison-Walker's new Research Center.

before being appointed district superintendent in charge of Ohio and Kentucky plants in 1928.

In 1931 he became manager of the Northwest Magnesite Company, Chewelah, Washington, and was elected vice president and general manager in 1938.

Mr. Garber then moved his headquarters to Pittsburgh in 1944, when he assumed the additional responsibility of Northwest Magnesite's new sea-water magnesite plant at Cape May, N.J.

He was elected a director and vice president and general manager of Harbison-Walker in January, 1947, and president and general manager in 1948.

Under his leadership, the company has carried on the greatest expansion program in its history, amounting to more than ninety million dollars of new construction and improvements.

It is for this reason that the new Research Center has been named in honor of Earl A. Garber, for his progressive spirit has long been a vital ingredient in the success of Harbison-Walker Refractories Company.

Glass Bubble Canopy in Tomorrow's Automobile?

In this article Dr. Ryan discusses the possibility of a glass canopy bubble for the car of the future. Technical problems are numerous but not insoluble; perhaps experience can be gained from work already done on plastic canopies in aircraft.

From time to time THE GLASS INDUSTRY will publish stimulating articles of this nature in order to illustrate the ever-increasing areas in which glass will undoubtedly play an important role.

by Dr. Joseph D. Ryan

GENERAL DIRECTOR, RESEARCH AND DEVELOPMENT

LIBBEY-OWENS-FORD GLASS COMPANY

• IN RECENT YEARS plastic bubble canopies have been employed as transparent enclosures on experimental automobiles of advanced design. Automotive manufacturers have frequently displayed such cars at their annual showing of new production models. The display of such models and the trend toward the use of larger and larger glass areas in production models logically leads to the question as to whether future production automobiles might not employ canopy passenger compartment enclosures.

Glass or Plastic?

If bubble canopies are to be used, will they be made of glass or transparent plastic either of which could result in the complete removal of roof supporting structures and provide the ultimate in sleekness and streamlining? Plastics which have been used experimentally, while suitable for aircraft use, still lack the important property of abrasion resistance and as well tend to craze and crack in relatively short periods of time under loads.

At the outset it should be recognized that automobiles, being earthbound, naturally subject any glazing material to much rougher usage than that experienced in an aircraft application. No presently known plastic has the requisite abrasion and permanence necessary for use as an automobile windshield where wiper action quickly makes the glazing unusable. Furthermore, rigid transparent plastic materials, unless laminated, tend to break up into large, sharp-edged fragments similar to plate glass even though requiring a greater amount of energy to rupture than does monolithic annealed glass. What, then, is the future for a glass bubble canopy?

How to Shape Glass Canopy?

One of the most serious obstacles to the near future development of glass canopies is the problem of shaping the glass to the bubble canopy configuration. Whereas plastic bubble canopies can be formed in the temperature range of 250 to 400°F, glass will require the use of temperature ranges in the region 1200-1500°F. To appreciate the enormity of this problem, one can to some extent borrow from experience in the forming of plastics into bubble canopies. Plastic canopies generally can be made by (1) the free blowing or vacuum blowing method which limits one to circular cross-sections, (2) stretch-forming over a male mold (holding the stretched sheet onto the mold by a fixture and then cooling), or (3) vacuum or pressure forming the plastic to any desired shape using the female mold and drawing the plastic sheet down to and in direct contact with the female mold over its entire surface. In all of the above processes, the thickness of the plastic sheet changes dependent upon the depth of draw designed.

As known to people experienced in the forming of plastic bubble canopies, extremely great care must be employed in the first step of the forming process which is heating the plastic sheet to a uniform temperature. It has been necessary to develop ovens which heat large sheets uniformly, controlling temperature over their entire area to ±5°F. Attaining similar temperature control in the 1200-1500°F area will present real but not insuperable difficulties. The forming of the glass sheets in the second step will require equally precise temperature controls including heating of the tooling and lastly a carefully governed cooling cycle to avoid breakage and to obtain proper annealing.

To function as a roof structure for an automobile, it is difficult to visualize, with our present knowledge, how one could successfully employ anything except a laminated glass canopy. Tempered glass would be unsatisfactory (cannot be used at present in windshields), so the problem of manufacturing an all-glass canopy is further complicated by the fact that two lites of glass of proper shape would have to be formed with the neces-

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Presented before the Society of Automotive Engineers, Detroit, Michigan, February 2, 1959.

LEAD SULPHIDE FILMS Part one

by Samuel Wein, CONSULTANT

In 1869, Dr. Reynolds, a Physician and Chemistry instructor in Great Britain first described the formation of "galena films" as early as 1869, and subsequently refined the process or technique with the efforts of Dr. Crubb, forming these films on glass, metals and other surfaces.

Walther, in 1896, described the reaction according to which sulphur of thiourea is split off when reacting with lead solutions (lead acetate and sodium hydroxide). The end products of this reaction are, cyanamide and lead sulphide.

It appears rather obvious, therefore, that the formation of lead sulphide films is by no means a new technique.

Hauser and Biesalsky, who published their experiments in 1910, are considered the inventors of the lead sulphide mirror formation, in which thiourea undergoes decomposition in the presence of an alkali and alcoholic solutions at ordinary temperatures. Hydrogen sulphide is given off.

The work done by Kast and Ehlinger, concerning the splitting off of the thiourea sulphur (desulfonation) was based on Walther's work. Their chief aims were to prepare photo-electric lead sulphide films and cyanamide.

Other Uses

Mirror makers confine their interests specifically to the deposition of lead sulphide films on glass for mirror use; little do they realize that the identical end product has other applications as well. It is not the intention of the author to describe fully these end uses; however, a review of the technical and patent literature reveals that the lead sulphide film has been used in such applications as the following.

Mirrors

In terms of quantity, undoubtedly the most important application of lead sulphide films is in the manufacture of "anti-glare" automobile reflectors. These mirrors are used, to a small extent in the home; they are also used, along with silver and gold mirrors, for contrast (color) in industrial decoration.

Lead sulphide mirrors are usually made in a room far away from the silvering process, because of their possible chemical effect (free sulphur) on the silver mirrors.

In the mirror industry, these lead sulphide films are referred to as "gun metal" and "galena" types.

Kempf finds that lead sulphide films adhere to glass surfaces 4 to 6 times better than silver films.

Photomechanical Methods

Heidenhain, Hawksley, also Colbert and Colbert make use of lead sulphide film on glass (and other surfaces) serving as it does the etch-resisting medium, a technique used in the planographic arts. One can imagine the degree of accuracy of this etch-resisting medium when lines as fine as 1 to 3/10,000 of an inch had actually been formed. Obviously, such a fine line can readily be used in diffraction gratings and as used in scientific devices and in scientific apparatus.

Resistance Elements

It is well established that the electrical resistance of lead sulphide films is high; hence, the application as a non-inductive resistance element of small cross sectional area. It must be borne in mind that these films possess unilaterial conductivity and that they likewise change their electrical resistance with other phenomena such as light, heat, and also with applied voltage. Where non-critical resistance elements (units) are to be used, lead sulphide films may be used to good advantage.

Capacity Effect

An interesting effect discovered by Putseiko was the variation of current in a lead sulphide film when it was placed in the field of two electrodes. If the source of E. M. F. is varied, as in an electrical condenser, the current change in the lead sulphide film likewise varies.

Thermoelectric Effect

A film of lead sulphide deposited between dissimilar metals in a grid forms a large active area within a small, confined space. When radiant energy (heat or light) affects the lead sulphide film, a source of E. M. F. is set up which can be measured on a galvanometer or micro-ammeter.

This thermoelectric effect was studied by Fuji, Hinterberger, Tied and Bruckman. Fuji reported that lead sulphide films had 3 to 5 times more sensitivity than thermocouples using Bi-Sb, Bi-Ag or Constantan-Manganin.

Rectifiers and Detectors

In the early days of radio (wireless telegraphy) receiving sets were equipped with *detectors*, usually galena natural crystals of lead sulphide. Subsequently, chemically deposited films were used.

Lead sulphide films deposited between dissimilar metals were also used as rectifiers for converting low-,

as well as high-frequency currents from A. C. to D. C.

Among the earliest references to lead sulphide as a rectifier is that of Mercadier in 1890, concerning *galena*, the natural crystalline form. Other pertinent works and literature are those of Amerikhanov, Bruckman, Colebrook, Davidenko, Fischer, Heineck, Hinterberger, Joffe, Lebedev, Luke, Schade, Schlede, Siemens and Demberg, Snelling, Trev, Tubandt and Haedicke, and Vrede.

Magnetic Effect

Croatto found a magnetic effect apart from the photo-electric effect of lead sulphide films in photo-electric cells.

Triode Effect

This effect is referred to by Banbury who studied the effect of a third, or control, element in the lead sulphide films.

Light Sensitive Cells

Types of light-sensitive cells include:

(1) Photo-conduction, in which a change in electrical resistance is exhibited on exposure to light;
(2) The so-called "barrier" type, in which an E. M. F. is generated without an external source of current.
(3) galvanic or "Becquerel effect" in which the film of lead sulphide in a suitable electrolyte will give rise to a source of E. M. F. on exposure to light.
(4) A pure photo-electronic effect, in which electrons are emitted from the surface as a result of light exposure.

Of the four described, photo-conduction cells are at present receiving the most attention by investigators. This type of cell, it has been found, has a much higher response to infrared rays between 1 and 3 microns thick than the present photo-electric types, and it is more easily made without expensive equipment.

Lead sulphide films of 1 micron thickness containing a slight amount of oxygen as an ordinary impurity were found to give a much higher response to light at lower light levels, according to James.

Dr. Cashman found that the lead sulphide photo-conduction cells compared with caesium photo-cells, exhibiting a much higher signal-to-noise output and a lower impedance. The cell noise was not increased in the presence of background radiation. The frequence response was excellent and the sensitive surface was undamaged by higher light levels.

As a result of the infra-red sensitivity of these cells, a directly heated exciter lamp has been developed which operates from an ordinary 60 cycle filament transformer. Radio frequency or direct current heating of the exciter lamp is thus not required.

The technical and patent literature lists the following investigators of the photo-electric effects of lead sulphide films: Anonymous, Baker, Bauer, Blackwell, Blackwell-Simpson and Sutherland, Case, Cashman, Dunaev and Maslavkovets, Dusault, Gibson, Gorlich, Heineck, Huxford and Platt, James, Kicinski, Kulper, Lange, Lee, Lee and Parker, Mercadier, Morton, Moss, Moss and Cashman, Pakswer, Schwarz, Sosnowski-Starkiewicz and Simpson, Sponable, Starkiewicz, Wilman, Wilson, Wilson and Cashman, Zworykin and Wilson, as well as Zhuse and Ryvkin.

Constructional design of photo-cells using lead sulphide films on glass is shown by Dr. Cashman.

Optical Filters

Thin or translucent films of lead sulphide, alone or in combination with other metal sulphides, are referred to by Colbert and Colbert, as well as by Morgan and Weinrich, who used these films as optical filters.

Spectral Response

Lead sulphide films have a peak response in the infra-red region, with most response being between 10,000 Å and 30,000 Å. Pakswer discusses the spectral sensitivity, electrical properties, and other related subjects.

Applications of the lead sulphide film to astrophysics, such as stellar photometry in the infra-red region, has been largely confined to the limitations set by the photographic plate type "Z" as well as the Cs-O-Ag photo-cell, both of which cut off at about 1.2 microns. This range is considerably increased by the use of the lead sulphide photo-cell, as explained by Kulper-Wilson and Cashman.

Osborn uses lead sulphide films as an infra-red detector aiding medical diagnosis.

Spectrometers

One company manufactures infrared recording spectrometers of several types using lead sulphide photo-cells.

Fire Detectors

Another company offers a photo-electric detector using lead sulphide films, termed cells, capable of reacting to a gas flame in a 2½" container at a distance of 10 feet. It is unaffected by overheat or bright sunlight.

Smoke Detectors

Sponable reports that the Case Research Laboratory, back in 1918, was able to detect a man smoking a cigar a mile away, which was quite an achievement at that time.

Burglar Alarms

The excellent infrared response of lead sulphide photo-cells offers advantages when used in burglar alarm systems, and controls of all kind using dark infrared radiation. The small size of these cells will offer advantages when the distance between the radiation source and the cell is short, which is generally the case on protective devices on machine tools. When longer distances are required, the circuits, optical systems and source must be designed to compensate for the smaller amount of radiant flux falling on the lead sulphide film.

It is recommended the same principles be used for other types of light-sensitive cells (emission types), according to Baker; that is, parallel beams for moderate distances, concentrated beams for short distances and modulated beams for long distances or for use where the level of extraneous illumination is high.

In this last application, it should be remembered that although the signal at constant radiant flux may be lower in the case of lead sulphide cells than in the case of the photo-emissive cells, the photo-conductive types

of cells have a considerable advantage in the signal-to-noise ratio, especially in cases where it is not possible to use vacuum tubes and high load resistors.

Counting and Sorting

Lead sulphide photo-cells and, in particular, double surface cell construction, according to Pakswer, are of particular interest in devices for photoelectric measurement, and counting and sorting of very small objects. In an industrial application at present under development, the cell is less than 10 mills.

Some applications may derive advantage from the fact that to date it has not been possible to manufacture a good end-on photo-tube with "S-1" response in a miniature bulb of approximately ¼ inch outside diameter. There is definitely a large field for a miniature end-on tube with infra-red response to work in conjunction with small incandescent lamps. Such cells could be used stacked in large numbers in tabulating machines, in electric signs with a varied design of text, and in all other similar applications where a configuration of holes in a continous band should be translated into electrical impulses.

The lack of a good photo-tube of miniature dimension is possibly one reason why a photo-electric phonograph pick-up has not become a popular product, although there have been many attempts to develop one. The photo-conductive lead sulphide cell seems to be a promising tool in this case too.

Sponable reports that in 1918 he was able to talk over a beam of light at a distance of some eight or ten miles. This was prior to the advent of commercial "talkies" and "radio". The system was then known as the "photophone."

Pakswer advises that these photophones were used in the United States, Britain and Germany in military optical telephony and telegraphy which could not be intercepted by the enemy, and could not be "jammed" like radio and radar.

Talking Motion Picture Sound Heads

There are at present three 16mm. sound projectors using lead sulphide photo-cells.

Surface Pretreatment

There are two common prerequisites in forming metal films on glass or other surfaces.

(1) The surface must be clean
(2) It must be "sensitized".

If the surface is not properly cleaned poor film formation will result—if at all.

Processes Outlined

The processes commonly used for forming lead sulphide films on any given surface depend on the reaction of a water-soluble lead salt in alkaline solution with a solution of thiourea.

In some of the techniques there is an immediate reaction between the compounds, evidenced by a darkening in the solution, with the formation of lead hydroxide which in turn is converted into the corresponding lead sulphide film. In other techniques the reaction is slow and the consequent lead sulphide film is built up with time; however, a uniform and metallic-appearing film of lead sulphide film will be seen on the glass surface if the solution is poured onto it. Without further treatment, the film is washed with running water and dried, and subsequently lacquered to prevent scratch.

Cleaning

Glass, and other surfaces, are usually cleaned with running water at room temperature. Many investigators add miscellaneous types of cleaning compounds to the water and subsequently rinse with running water. These cleaning compounds are usually alkaline and contain sodium hydroxide. There are many proprietary (commercial) compounds available that are ideal for this purpose. One that the author uses contains:

Sodium hydroxide	50 grams
Sodium gluconate	50 "
Water	1 gallon

This solution has the tendency to "wet" the glass surface, so that film to be deposited will adhere correctly. Further, no chemical deposits are formed on the glass when such cleaning techniques are used.

It is important to remember that the surface *must be* rinsed with copious amounts of water, immediately after it has been chemically cleaned.

Sensitizing

There are two schools of thought in regards to lead sulphide film formation making use of sensitized surfaces. The early investigators certainly did not use sensitized surfaces because the technique was not known.

It is now common knowledge that sensitized surfaces create a far better and faster reaction with the lead compound during the processing, and because it gives rise to a much warmer film. A review of Sensitizing techniques is given by Wein in an earlier issue of THE GLASS INDUSTRY. One such solution may be made by dissolving 20 grams of tin chloride to the gallon of water. Sufficient hydrochloric acid is then added to this solution to clarify it; i. e. until the solution is no longer hazy or milky.

This solution without the addition of hydrochloric acid will last but one day (maximum), whereas the addition of the hydrochloric acid will increase its lasting properties to weeks without showing signs of deterioration.

In the sensitizing process the prepared solution just described is poured onto the given surface and allowed to remain in contact with that surface for about 30 seconds. A longer period of time will serve no useful purpose. It is then rinsed with running water.

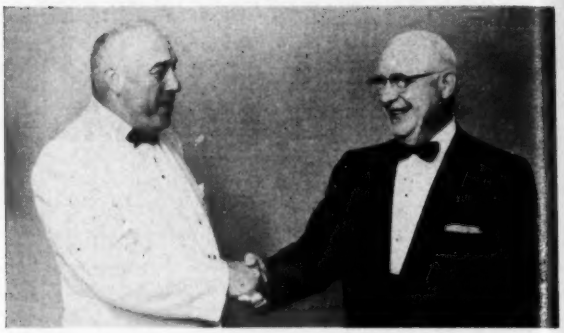
The surface may also be sensitized by soaking it in a tank containing this solution, followed of course by rinsing. A third technique is by spraying the sensitizing solution, and rinsing afterwards.

As in the case of other techniques for forming metal films on glass or other surfaces, care must be exercised not to touch the surface once it has been sensitized; otherwise, it will have to be recleaned and re-sensitized.

Once the film of lead sulphide has been formed, irrespective of the technique or process used to form it, it

(*Continued on page* 393)

GCMI Annual Meeting



Fred N. Dundas (left), new GCMI president, receiving congratulations from outgoing president Glenn A. Mengle of Brockway Glass Co. Mr. Dundas is executive vice president of Dominion Glass Co. Ltd.

• FRED N. DUNDAS, executive vice president, Dominion Glass Company Limited (Montreal), was elected president of the Glass Container Manufacturers Institute during the annual membership meeting at The Greenbrier, White Sulphur Springs, West Va., from May 19 to 22. He succeeds Glenn A. Mengle of Brockway Glass Company.

F. S. Heuisler, Maryland Glass Corporation, became first vice president, and C. G. Bensinger, Owens-Illinois Glass Company, second vice president. Four vacancies on the board of trustees were filled by J. Gordon King, Hazel-Atlas Glass division, Continental Can Company (re-elected); G. F. Collins, Jr., Liberty Glass Company; James G. Ferguson, Laurens Glass Works, Inc.; and E. M. Terner, Metro Glass Company (each elected for a first term).

George F. Collins, Jr. (right), Liberty Glass Co., and new trustee of GCMI, discussing three-day meeting with Joseph C. Feagley (center), Armstrong Cork Co., and Royden C. Blunt, Buck Glass Co.

Mr. Dundas has been a leader in GCMI activities for many years, having been a vice president and secretary in 1955, executive vice president in 1956 and, later that year, a director. He became a trustee in December, 1956, and has served as a vice president for the past two years.

Committee reports were presented in such areas as Market Research and Promotion (J. W. Fisher); Progress Report (R. L. Cheney); Advertising and Promotion for 1959 (Bush Barnum and Denning Harvey) and New Markets (Ford Sammis).

Several technical groups assembled to discuss GCMI activity: Testing Procedures (Dr. R. S. Arrandale, Thatcher Glass Manufacturing Company, chairman, with Dr. L. G. Ghering and Dr. R. E. Mould of Preston Laboratories); Glass Packed Products (Chairman Raymond Wells, Armstrong Cork Company; R. E. Wirth, Ball Brothers; and R. N. Maxson, GCMI Packaging Research Laboratory).

A. J. Martin gave a report on the Committee concerned with Labor Relations; A. F. Huni discussed activities of the Traffic Committee; and S. L. Rairdon described the work of the Sub-Committee for Public Education.

Left to right: S. B. De Merell, Anchor Hocking Glass Corp.; Fred E. Fuller, GCMI general counsel; John M. Foster, Foster-Forbes Glass Co.; and Howard C. Herger, Pierce Glass Co., studying new light-weight glass beer bottle now available in several eastern markets.

GCMI program committee which arranged activities of GCMI annual meeting at The Greenbrier in White Sulphur Springs, W. Va. Left to right: E. D. Easterby, Laurens Glass Works; Chairman Herger, Pierce Glass; and J. Gordon King, Hazel-Atlas Glass division.

Russian Translations of Interest to the Glass Industry

Temperature Dependence of the Viscosity of Silicate Glasses

By M. Kh. Karapet'yants
MENDELEEV INSTITUTE OF CHEMICAL TECHNOLOGY, MOSCOW

VISCOSITY η IS ONE OF the fundamental physicochemical properties of glasses. Experimental determination of the η of molten silicates is difficult because of the high temperature involved and the very wide range of the η values. A theoretically established relationship between η of glasses and temperature does not exist; thus, it is understandable why so much effort was put into empirical correlations between temperature and η of glasses.

Many equations (some of these were specifically derived for glasses) and nomograms[1] were suggested for the computation of the temperature dependence of viscosity. No evaluation of the equations found in the literature is attempted here, but it may be stated that certain deficiences are apparent, also in those which agree with the experimental data within the limits of precision determined by the possible non-uniformity of the melt, by the errors in the calibration of viscometers, by inexact temperature measurements, and so on. In general, application of these equations in a wide temperature range is impossible without some loss of precision and necessitates a previous determination of empirical constants which makes the computation laborious and sometimes impossible (because of lack of experimental data). Also it is not always possible to correlate the equation constants with the composition of the glasses.

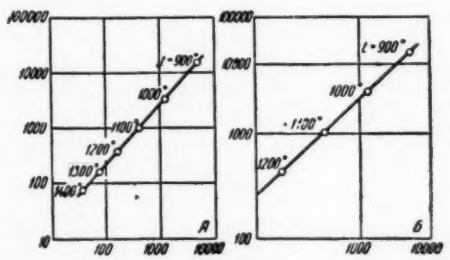


Fig. 1. Relation between the temperature dependences of viscosity (in poises) of the glasses $Na_2O.2SiO_2$ (M) and $Na_2O.3SiO_2$ (N). A: distorted temperature scale. B: regular temperature scale.

Methods of comparative calculation of properties were presented earlier[2], and a variation of these methods was tested for the instance of heat evolution observed in several processes[3]. In the following, one of these methods is applied to the temperature dependence of η. For η of a glass under study (denoted by η_N) and that of a reference glass (η_M), an approximate linear equation

$$f(\eta_N) = Af(\eta_M) + B \qquad (1)$$

may be written; it compares the two viscosities according

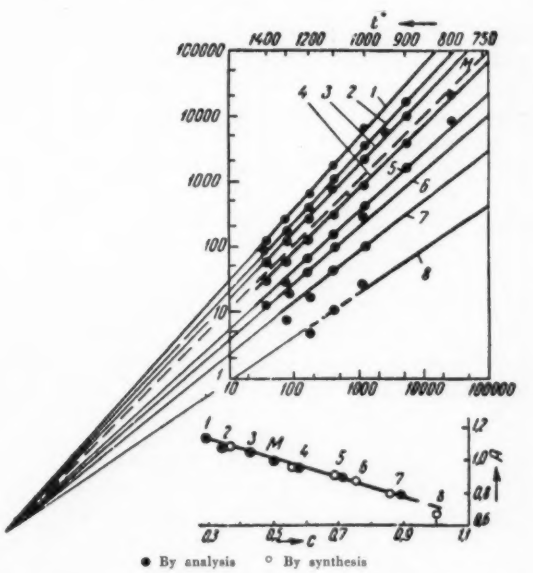
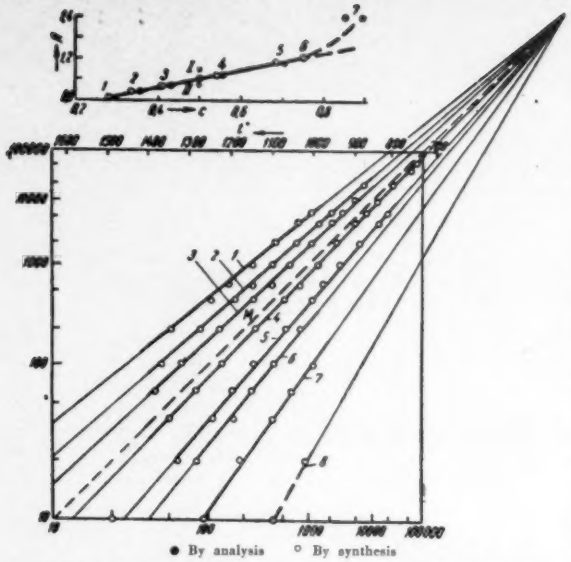


Fig. 2. Temperature dependence of viscosity (in poises) of the glass $Na_2O.2SiO_2$ (M) and of several other glasses in the $Na_2O - SiO_2$ system. 1: 22 mol. per cent Na_2O (by synthesis); 2: 25 per cent Na_2O; 3: 29 per cent; 4: 35 per cent; 5: 40.7 per cent; 6: 42.8 per cent; 7: 46 per cent; 8: 50 per cent. In the lower right corner, the dependence of the coefficient A of equation (2) on the molar ratio $c = Na_2O : SiO_2$.

A slightly condensed translation from *Steklo i Keramika 15*, No. 1, p. 22-25 (1958).



● By analysis ○ By synthesis

Fig. 3. Temperature coefficient of viscosity (in poises) of the glass Na_2O. 2 SiO_2 (M) and of several other glasses in the Na_2O – SiO_2 system, coded as in Fig. 2. In the upper left corner, the dependence of the coefficient A of equation (3) on the molar ratio c. I: Babcock's data. II: Preston's data.

to functional scales. Relation (1) will give results more exact, the more similar the two compounds. Hence, if M and N are glasses similar in their properties and their structure, equation (1) ought to give satisfactory agreement with the experiment.

As equation (1) implicity expresses the dependence of η on temperature t, the form of the function f is determined by the η-t relation. If we set $f(\eta) = \log \eta$; that is, if we start from the approximate equation

$$\log \eta_N = A \log \eta_M + B, \qquad (2)$$

we obtain a distorted temperature scale.

This is demonstrated in Fig. 1 A. Points plotted according to the double-log scale of viscosities are lying on a straight line. (The experimental data are taken from literature[4]).

If, on the other hand, a uniform temperature scale is used, equation (1) is valid if the coordinate of viscosities is distorted. This is shown in Fig. 1 B. In this instance relation

$$t_N = At_M + B \qquad (3)$$

is more convenient to use than equation (1); in (3) the temperatures of the two liquids, at which their viscosities are equal, are compared. Equation (3) is an inversion of equation (2).

The condensation of the viscosity scale (Fig. 1 B) in the region of large η values and the corresponding extension of the temperature scale (Fig. 1 A) are caused by the rapid increase of viscosity at low temperatures. It may be noted that equation (2) does not follow from simple exponential equations as can be seen from the distribution of the points on the straight line of log η_N versus log η_M, see Fig. 1 A. This is an indirect indication of the variation of the energy of activation of the viscous flow of glasses with temperature variation.

Equation (3) may be considered an extension of the Duehring equation for vapor pressure to viscosity[5]. It also corresponds to the relation between η and the temperature expressed on a functional scale as proposed in Irany's[6] and Slavyanskii's[7] papers.

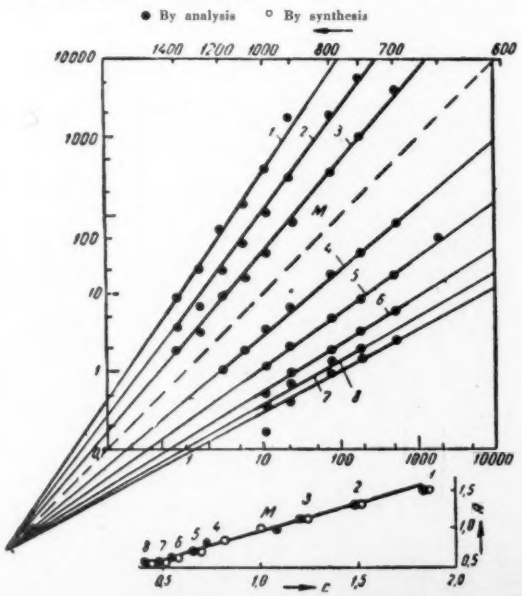
As mentioned earlier, extension of the method of comparative calculation from two to several substances belonging to one group markedly expands computation possibilities. This is true, in particular, in reference to expression (1) and to equations (2) and (3).

Transition to the computation of the viscosity of several compounds is shown in Figs. 2 to 5. Figs. 2 and 3 refer to the system Na_2O - SiO_2, the former corresponding to equation (2) and the latter, to equation (3). Figs. 4 and 5 present analogous graphs for the system PbO - SiO_2, based on literature data[8]. Contrary to Fig. 1, the temperature scale is plotted along the top of Figs. 2 to 5.

It is clear from these graphs that the majority of the points are situated along straight lines within the limits of the experimental error[9]. We note also that the fact of the compounds being mutually related is indicated by the fanning of all curves from approximately one point[10]. Thus, if the position of this point and the η-t relation of a reference substance are known, the temperature dependence of the viscosity of another glass of a known composition can be found as soon as the value of η at any one temperature is known.

The regularity in the properties of the substances compared is demonstrated by the monotonous variation in the slope of the lines of Fig. 2 to 5 with the glass composition. This variation is well shown in the small graphs (lower right corner of Figs. 2 and 4 and upper left corner of Figs. 3 and 5) representing the coefficient A of equations (2) and (3) as a function of the composition of the systems studied. There are no systematic deviations; those observed (which are moderate also in the range of supercooling) presumably are caused by experimental errors and by inexact determination of the chemical composition of the glasses rather than by low precision of the computing method.

Fig. 4. Temperature dependence of viscosity (in poises) of the glass PbO. SiO_2 (M) and of several other glasses in the PbO – SiO_2 system. 1: 35 mol. per cent PbO (by synthesis); 2: 40 per cent; 3: 46 per cent; 4: 55 per cent; 5: 60 per cent; 6: 64 per cent; 7: 66.7 per cent; 8: 70 per cent. In the lower right corner, the dependence of coefficient A on molar ratio c = SiO_2: PbO.



The crossing of all straight lines in one point and the regular variation in their slopes permits us, in many instances, to estimate the temperature dependence of the viscosity of glasses which have never been studied. Thus, the graph printed in the upper left corner of Fig. 3 shows that a value $A = 1.08$ corresponds to $c = 0.6$. If a line corresponding to this value of A is drawn in the graph of η versus η_M (Fig. 3), the temperature dependence of the viscosity of this glass is immediately obtained for the range 750°-1400°C.

Determinations of this kind can be carried out also analytically with the help of an equation combining the relations "η_N versus η_M" and "A versus c". It is seen from Figs. 2 to 5 that the additivity rule is satisfactory for a wide concentration range; that is, a linear relationship of the type

$$A = a + bc \qquad (4)$$

may be used.

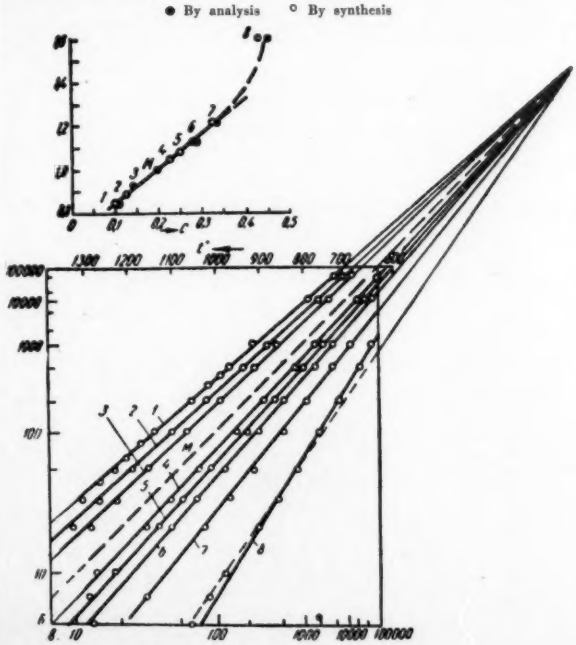
It also becomes possible to select the most trustworthy data on the temperature dependence of viscosity. Thus we may conclude from Fig. 3 that the viscosity data of $Na_2O.2\,SiO_2$ advocated by Preston[11] and Babcock[12] are unreliable, contrary to those of Sharsis.

The above-mentioned methods for viscosity calculation may be extended also to more complex systems. If, for instance, ternary systems are studied, cross-sections corresponding to a constant concentration of one of the components should be considered; see, for instance, Fig 6 constructed according to literature data[13].

Extension of expression (1) from two to several related compounds permits application of another method of comparative computation. This method earlier[14] was considered for heat effects and, when applied to viscosity, leads to equation

$$f(\eta_{t2}) = Af(\eta_{t1}) + B \qquad (5)$$

Fig. 5. Temperature dependence of viscosity (in poises) of the glass $PbO.SiO_2$ (M) and of several other glasses in the PbO – SiO_2 system, coded as in Fig. 4. In the upper left corner, the dependence of coefficient A on molar ratio $c = SiO_2$: PbO.



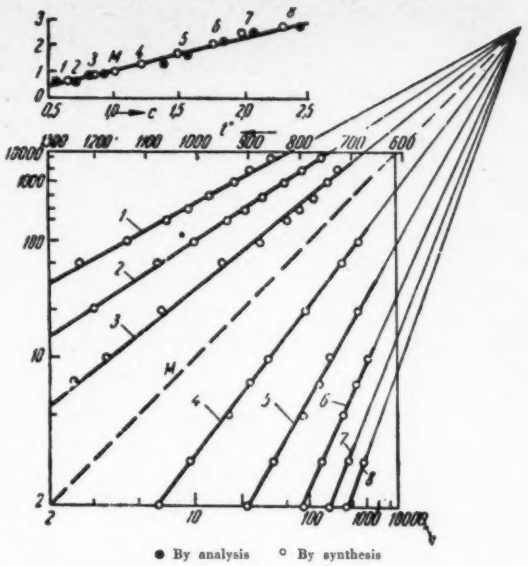


Fig. 6. Temperature dependence of viscosity (in poises) of the glass SiO_2 60 per cent, PbO 28.6 per cent, Na_2O 11.4 per cent (M) and of several other glasses in the system SiO_2 + 28.6 per cent PbO + Na_2O. 1: 65 mol. per cent SiO_2 (by synthesis) + 6.4 per cent Na_2O; 2: 63.5 + 7.9 per cent; 3: 62.5 + 8.9 per cent; 4: 58.2 + 13.2 per cent; 5: 57.2 + 14.2 per cent; 6: 56.0 + 15.4 per cent; 7: 53.9 + 17.5 per cent; 8: 50.0 + 21.4 per cent. In the upper left corner, the dependence of the coefficient A of equation (3) on the molar ratio $c = Na_2O$: SiO_2.

in which the viscosities of a series of related compounds are compared at two different temperatures. In this instance both equation

$$\log \eta_{t2} = A \log \eta_{t1} + B \qquad (6)$$

and the equation corresponding to relation (3) may be applied.

If several temperatures, rather than only two, are involved, straight lines will be obtained which, when extrapolated, will cross in the points identical with those derived from equations (2) and (3). The graphs thus obtained will represent the result of cutting graphs such as shown in Figs. 2 to 6 by vertical lines. It should be noted that the precision of the calculation based on the six above relations may be different in every case.

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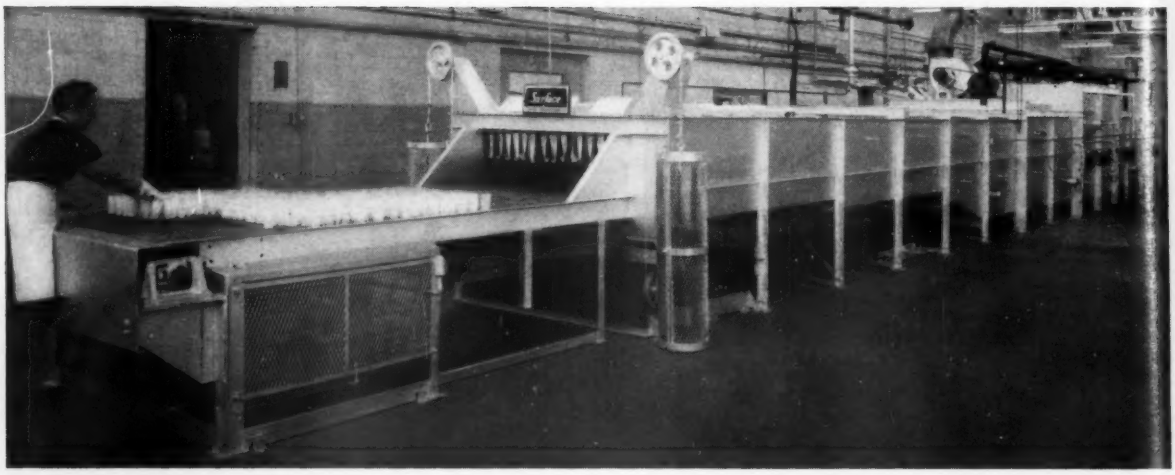
a "useful life" can cost you money

Depreciation policies based on the useful physical life of equipment have lulled many companies into dangerous complacency. By ignoring inflation and technological obsolescence, they pay dividends and taxes on profits which don't really exist.

Inevitably, they discover that their depreciation reserves are inadequate to replace worn out or obsolete equipment.

However, aggressive managements have found two alternatives to that dilemma. First, they prove to the Government that their depreciation rates should be based on the economic—not the physical—life of their equipment.

Second, they purchase equipment which will recoup their investment within its economic lifetime. This is the factor which prompts many companies to specify Surface Combustion lehrs, kilns, and ovens.



This radiant tube decorating lehr is recouping its owner's investment.

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NEWS in The Glass Industry

Stewart Lang Joins Owens-Illinois

Stewart M. Lang, ceramist and authority in high-temperature research, has joined the Fundamental Research Section of Owens-Illinois Glass Company, where he will be in charge of a group working in the field of temperatures above those now used in glass production.

Mr. Lang has been senior ceramist at Nuclear Materials and Equipment Corporation in Appolo, Pa., for the past two years. He supervised the development and fabrication of uranium dioxide and other ceramic nuclear fuel materials.

Previously a member of the Minerals Products Division of the National Bureau of Standards in Washington, D. C., for 10 years, he served as assistant chief of the engineering ceramics section and worked on high-temperature reactions of ceramic oxides for application in jet engines, rockets, missiles and nuclear installations. In February 1957 he was presented with the U.S. Department of Commerce's Silver Medal Meritorious Service award for his work.

Mr. Lang has also been consultant to the Division of Research, the Naval Reactors Branch of the U.S. Atomic Energy Commission, and the Materials Laboratory at Wright Air Development Center, Dayton, O.

At Owens-Illinois, he will study the physical, chemical and thermodynamic properties of known materials, and the synthesis of new materials, under the influence of very high temperatures. Since this work will be done in relatively unknown scientific areas, at temperatures that could reach as high as 10,000° to 30,000°, he will design and construct his own apparatus and measuring devices.

Iroquois Glass Starts Production

Iroquois Glass Limited's new plant at Candiac, near Montreal, Canada, has begun production after a 39-week construction period.

The $5-million plant, which produces flint, green and amber containers at a rate of 300,000 units a day, has fully automatic mixing and batch-feeding equipment. The company is expected to employ 275 persons when it reaches full capacity.

John Wargo Retires from Knox

John Wargo, superintendent of glass production at Knox Glass' Sheffield, Pa., plant has retired after more than 60 years of service.

Mr. Wargo began as a laborer in the Sheffield plant in 1898, at ten years of age. He became foreman eight years later and in 1923 assumed his most recent post of superintendent. A banquet was held in his honor on May 26, during which Dr. A. W. Wishart, president of Knox Glass, presented him with a television set in recognition of his services.

Stewart M. Lang

R. C. Conover

H. K. Porter Appoints Conover

R. C. Conover has been appointed manager of H. K. Porter Company's Western District. Mr. Conover will supervise operations of company plants in St. Louis, Mo.; Bessemer, Ala.; Attawa, Ill.; and Canon City, Colo.

Mr. Conover served as assistant superintendent of Harbison-Walker Refractories Company's East Chicago Works and superintendent of their Hays Works from 1932 to 1941. He joined Emsco Refractories Company in 1942 and put their new Lehi, Utah, plant into operation. He became production manager in 1944 when this plant was purchased by Gladding-McBean and Co. and rose to vice president of manufacturing and vice president and general manager of the pipe products division of Gladding-McBean.

Fischer & Porter Forms Fiberglass Co.

A new company, Warminister Fiberglass Company, has been formed by Fischer & Porter Co., for the production of fiber glass reinforced plastic parts. The firm is independent of the parent organization. Robert Tomlinson has been named manager.

Fischer & Porter manufactures glass products, flowmeters, industrial instruments and data reduction and automation systems.

John Wargo

Robert I. Tomlinson

Dr. Joseph D. Ryan

Dr. Roy W. Wampler

Ryan, Wampler in Top Research Posts—LOF

Dr. Joseph D. Ryan has been appointed general director of research and development for Libbey-Owens-Ford Glass Company. Dr. Roy W. Wampler has become director of research.

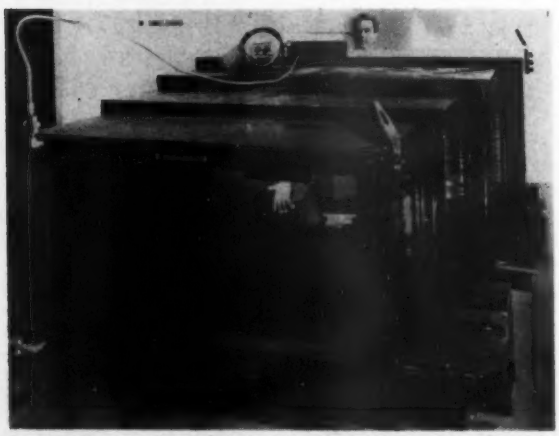
Dr. Ryan has been associated with LOF since 1931 and was formerly director of research. At one time he was an instructor in the Department of Chemistry at the University of Michigan, and in 1939 was admitted to practice before the U. S. Patent Office. He holds several patents in the area of safety and flat glass.

Dr. Wampler, who succeeds Dr. Ryan as director of research, taught chemistry at Kansas State College before entering industrial research. He has been a member of the research department since 1929 and has done a great deal of work in laminated safety glass and Thermopane insulating glass.

Luckenbach Promoted by Foote Minerals

W. Frederick Luckenbach, Jr., has been named general manager for the new commercial development department of Foote Minerals Company. The department is responsible for introducing new products and adapting existing ones to new uses.

Mr. Luckenbach has been associated with Foote Minerals for ten years serving in sales and research; he has been manager of chemical sales since 1954.



Corning Glass Works' 8½' thick radiation shielding window assembled for the Atomic Energy Commission. An expanded viewing area is provided by high index of refraction of the glass which appears to "stretch" the man's arm.

Brockway-Tygart Valley Merge

The stockholders of Brockway Glass Company and the Tygart Valley Glass Company have approved a merger that will make Brockway the fourth largest glass container manufacturer in the country.

The Tygart Valley Glass Company will be operated as a wholly-owned subsidiary of Brockway on a stock dollar-for-dollar transfer of ownership. Common and preferred stocks will be exchanged in proportion to the ratio held by Brockway stockholders.

Testing Ceramics For Atomic Fuel

Dr. H. W. Newkirk, a physical-inorganic chemist, and B. B. Brenden, an optical engineer, have designed a carbon arc image furnace to test atomic fuel element materials. The two General Electric scientists are working at the Atomic Energy Commission's Hanford, Wash., plant on the development of ceramic fuel elements.

The furnace uses the same principle as that of a magnifying glass which is used in lighting a fire. Light rays from an air-blown, water-cooled carbon arc are reflected from a parabolic mirror in one end of the furnace to another such mirror in the other end. The second mirror focuses the light rays on a specimen placed inside a quartz envelope containing a helium atmosphere. Steam can be added to the atmosphere to approximate conditions inside a reactor when a fuel element ruptures.

Moving or still pictures of the specimen can be made while it is being heated. During all phases of the experiment, the specimen can be observed through microscopes, and photographs can be taken in black and white or in color.

Such observation is important since high-temperature behavior of fuel elements inside a reactor is the key to higher power levels. The furnace creates temperatures as high as 5,000°F.

Ceramic fuel elements show great promise for reactors because they can withstand high operating temperatures.

Corning Assembles 8½-Foot Radiation Window

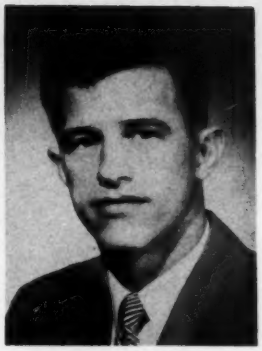
Corning Glass Works has assembled an eight-and-one-half-foot-thick radiation shielding window for the Atomic Energy Commission.

Designed to protect persons observing activity in a radioactive shop of 320 x 234' dimensions, the nine-ton window will be installed at the National Reactor Testing Station near Idaho Falls, Idaho.

The window contains seven separate glass panes, each nine inches thick, and 12 clear plastic sheets housed in a steel frame and charged with oil. It measures 31 x 64 inches on the "hot" side and 22 by 42 inches on the viewing side.

This type of window has found extensive use in atomic research and is being used in the U.S. Navy's atomic submarines as "peepholes" into radioactive compartments.

John R. Alles



Frank Van Kirk

Bernard L. Schoolcraft

R. H. Barnard, Jr.

Alles Named Ass't Manager by Ball Bros.

John R. Alles has been appointed assistant manager of Ball Brothers Company's new glass container plant now under construction at Asheville, N. C.

He became associated with Ball Brothers in 1942 and has since held the posts of junior engineer in mold design, senior mechanical engineer, and estimator and cost analyst of general engineering and construction projects.

Norelco X-ray School

The thirty-fourth Norelco X-ray School of Philips Electronics, Inc., devoted entirely to the subject of X-ray Spectrography, will be held at the Sir Francis Drake Hotel, San Francisco, California, during the week of August 31.

Ohio Plate Glass Executive Promotions

R. C. Heymann, Sr., formerly president of Ohio Plate Glass Company, has become chairman of the board and chief executive officer. R. C. Heymann, Jr., vice president and secretary, is now president; C. T. Perdue, executive vice president, becomes secretary and P. F. Heymann, vice president, becomes vice president, glass division.

Robert Shaul has been appointed sales manager of the glass division for the Ohio, Michigan and Indiana territory.

Schmidt and Little Appointed by Chrysler

R. P. Schmidt and H. J. Little have become manufacturing manager and production superintendent, respectively, at Chrysler Corporation's new McGraw Glass Plant. Mr. Schmidt will be responsible for the administration of manufacturing programs while Mr. Little is in charge of glass fabrication.

Mr. Schmidt, who has been associated with Chrysler since 1954, was manager of manufacturing services in the Parts and Equipment Manufacturing division prior to his present appointment.

Mr. Little was associated with Chrysler Corporation's Dodge division from 1934 to 1940 and served as plant superintendent for the Guardian Glass Co. before his new appointment. The new plant is expected to start production in January of 1960.

Fiberglass Appointments at Johns-Manville

Frank Van Kirk has been appointed manager of Johns-Manville Fiber Glass' plant in Parkersburg, W. Va., Bernard L. Schoolcraft has been promoted to manager of plant 2A and 2B and R. H. Barnard, manager of plant 2C in Defiance, Ohio.

Mr. Van Kirk, with Johns-Manville since 1949, was manager of the Navy flotation wool department in 1951 and was promoted to production manager in 1952 and manager of plants in 1955.

Mr. Schoolcraft, formerly superintendent of the glass department, has been with Johns-Manville since 1951.

Mr. Barnard served as industrial engineer at the J-M Waterville plant and sales representative in the Charlotte, N. C., area. He was formerly superintendent of Plant 2C.

The three J-M Fiber Glass plants in Defiance produce fiber glass blanket insulation, home insulation and marine board (Plant 2A); pipe insulation (Plant 2C) and an insulation fabricating division and warehouse storage (Plant 2B).

St. Gobain Furnace has Record Run

American Saint Gobain Corporation's furnace No. 2 at Okmulkee, Okla., recently finished a six-year and three-month period of operation, producing 175,690 tons of glass. During this period the furnace was given two hot repairs which kept it out of production for a total of four weeks.

R. P. Schmidt

H. J. Little

Kenneth A. Gibson

Charles E. Stroud

Pittsburgh Plate Names Plant Managers

Kenneth A. Gibson and Charles E. Stroud have been appointed managers of Pittsburgh Plate Glass Company's plants at Crestline, Ohio, and Creighton, Pa., respectively.

Mr. Gibson has been with Pittsburgh Plate since 1949 and has served the past five years as manager of the Creighton plant.

Mr. Stroud, who succeeds Mr. Gibson at the Creighton plant, has been with Pittsburgh since 1925. He was formerly production engineer for fabricated products in the company's general office in Pittsburgh, Pa., and subsequently held supervisory positions at the Ford City and Creighton plants.

Land Pyrometers to be Handled by Atlantic

Atlantic Pyrometers, Inc. has been appointed by Land Pryometers Ltd., of Sheffield, England, to handle United States sales of three of their new pyrometers known as the glass surface and suction Pyrometers.

Owens-Illinois Promotes Two

Bruce A. Demers has been promoted to administrative manager of Owens-Illinois Glass Company's glass container plant near Bogota, Colombia. George E. Ott will succeed Mr. Demers as supervisor of the tabulating department at the company's Toledo, O., plant.

Mr. Demers will handle purchasing, personnel and accounting at the Colombia operation. The plant is being rehabilitated and is expected to begin production early next year.

New Uses for Vycor Glass

Corning Glass Work's Vycor glass is being used in new high-temperature applications for welding torches and protective tubing for thermocouples.

The 96 per cent silica glass, in the form of transparent nozzles, is used on inert glass-welding torches where temperatures approach 2,400°F. With an inside ground joint, which eliminates the need for a gasket, the nozzles fit over the welding point, allowing free flow of gas to the spot of the weld. The transparency permits the welder to see his work.

Porter Appoints Vervaeke

R. G. Vervaeke has been appointed manager of H. K. Porter Company's Pascagoula Works, replacing W. R. Shaw, who resigned on May 1.

British Glass Workers Visit U. S. Manufacturers

A group of British glass workers visited the United States late last month on a two-week tour (June 16-July 1) of the glass container and fiber glass industries. They were here on invitation of the Glass Bottle Blowers Association of the United States and Canada, which latter group had two years previously, in 1957, toured the glass industry in Great Britain.

Headed by Sir Thomas Williamson, the eleven visitors arrived in New York on June 16 following a 7½-hour jet flight from England and that evening were guests of the GBBA at a dinner in the Hotel Astor, New York.

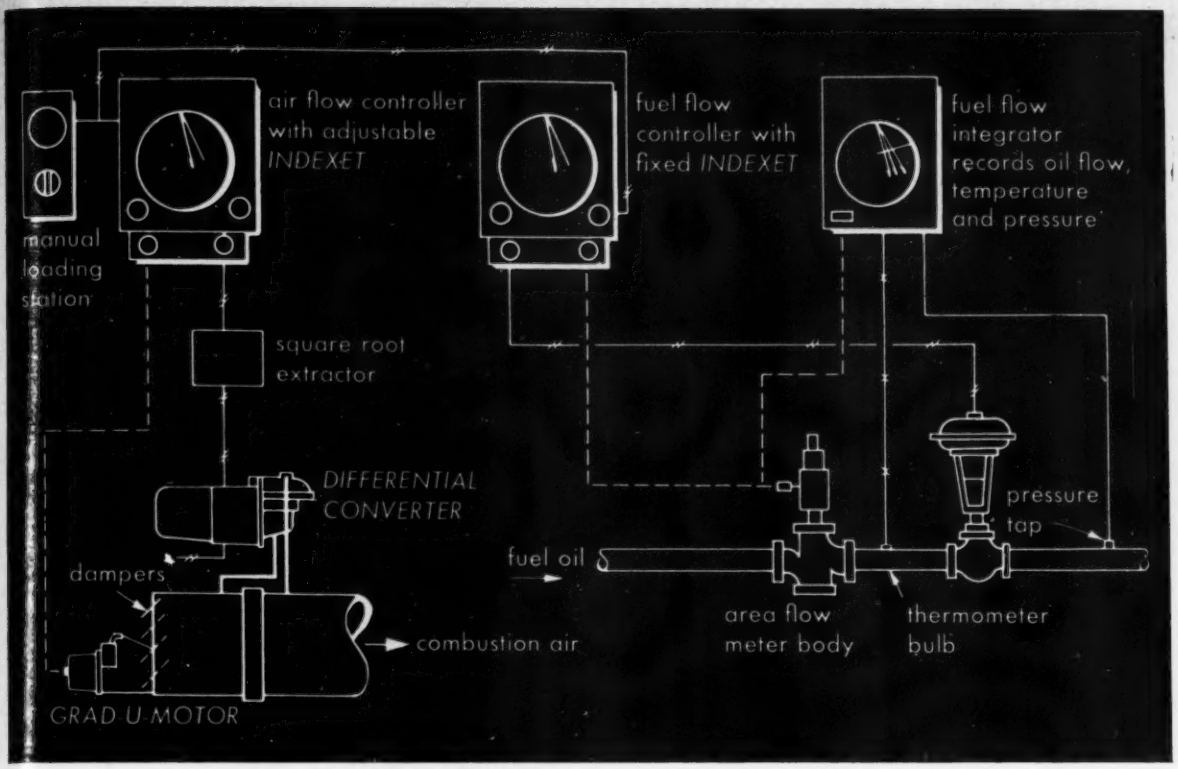
Raymond H. Dalton, international vice president of the Glass Bottle Blowers Association, extended a warm welcome to the glass men and reported that the American glass companies had offered excellent cooperation in setting up the two-week program.

Lee W. Minton, GBBA international president, commented that this exchange of information and reciprocal-visit program was part of the "people-to-people" project, the purpose of which is to create a deep warmth and understanding among the nations of the world.

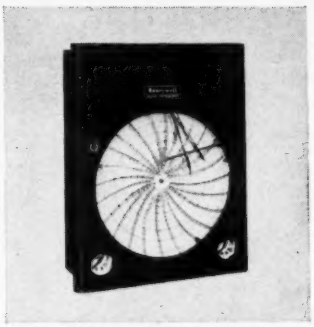
Speaking for the group, Sir Thomas expressed his country's appreciation for the contribution America made to British production following the second world war. "The United States," he continued, "has become the greatest producer in the world and has opened its doors to industry overseas so that we can see how you do things." He expressed the hope that this feeling of cooperation would continue to strengthen.

Other members of the group were A. Fox, glass bottle machine operator; T. J. Spooner, sorter; S. McQuillan, glass blower; W. J. Aldridge, sorter, box hand, batch dept. on furnaces; W. Brandon, sorter; J. Cooper, national chairman of the National Union of General and Municipal Workers of Great Britain; C. Smith, national executive committee representative; J. R. McLoughlin, Liverpool and Irish district secretary; H. E. Matthews, national industrial officer; and C. M. Scott, publicity officer.

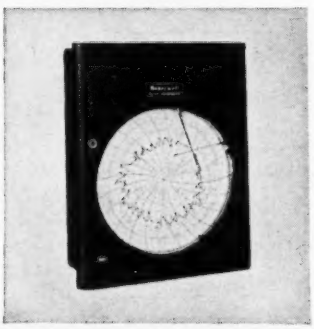
Among the glass companies visited by the men were Diamond Glass Co., Royersford, Pa.; T. C. Wheaton Glass Co. and Armstrong Cork Co., Millville, N. J.; Owens-Illinois Glass Co., Bridgeton, N. J. and Atlanta, Ga.; Anchor-Hocking Glass Co. and Gaynor Glass Works, Salem, N. J.; Kimble Glass Co., division of Owens-Illinois, Columbus, O.; Owens-Illinois Technical Center, Toledo, O.; Johns-Manville Fiber Glass Inc., Waterville and Defiance, O.; Foster Forbes Glass Co., Marion, Ind.; and Thatcher Glass Manufacturing Co., Lawrenceburg, Ind.



Fuel-air ratio control system. **Air flow and fuel flow controllers are equipped with adjustable and fixed *Indexet* mechanisms which move set point index up or down scale to provide the most efficient ratio of air to fuel for any given flow condition.**



1. Electric recording fuel flow meter with pneumatic control. If desired, it can be equipped with integral external by-pass panel.



2. Recording integrating flow meter with additional pens for temperature and pressure measurements.

Save fuel with Honeywell fuel-air ratio tank control

Honeywell controls step up furnace efficiency, save fuel on every ton of glass produced. Precise control of fuel-air ratio, biased by O_2 measurement, maintains atmospheres that increase furnace life and keep glass color uniform. It eliminates the need for frequent control readjustments to compensate for air infiltration changes which occur during the furnace campaign. Another feature of the system readmits fuel and air at controlled rates for minimum thermal loss following reversal.

Honeywell instrumentation is custom-matched to your process, with controls that prove themselves time and again in countless glass tank applications. Along with the inherent advantages of the fuel-air ratio control system and the individual instruments that comprise it, you get all of the many valuable services that come with Honeywell instrumentation.

Get complete details from your nearby Honeywell field engineer. Call him today . . . he's as near as your phone.

MINNEAPOLIS-HONEYWELL, Wayne and Windrim Avenues, Philadelphia 44, Pa.

Honeywell

First in Control

Part of exhibit in Museum of Glass which was dedicated May 28 in Tel Aviv, Israel. This collection, which traces history of 3,500 years of glass making, is considered one of finest in the world.

Museum of Glass Opens in Tel Aviv

The Museum of Glass, which houses the million-dollar glass collection of the late Dr. Walter Moses, was dedicated in Tel Aviv, Israel, on May 28. The collection, regarded as one of the finest in the world, traces the history of 3,500 years of glass making. It is divided into five general periods: The making of glass before the glass-blowing art had been developed (1500 B. C.-100 B. C.); The Roman Period (100 B. C.-300 A. D.); Byzantine glass (300-600 A. D.); glass making in the Arabic Period (600-1500 A. D.); European and American glass (1500 A. D.-present).

President Ben Zvi of Israel, guest of honor at the dedication, delivered the principal address.

The new building for the glass museum was made possible by a gift of the late Louis M. Rabinowitz, of New York, to the American-Israel Cultural Foundation which was added to the funds and land made available by the city of Tel Aviv.

The museum building, itself, is the first of 14 structures planned for the Museum Ha'aretz (The Museum of the Land) which will comprise "The Archaelogical Museum of Tel Aviv." The entire collection of more than 10,000 archaelogical objects, will be associated with the Archaeological Institute of the Tel Aviv University.

Westinghouse Appoints McNall

Dr. John W. McNall has been appointed director of research for the Westinghouse lamp division, succeeding E. G. F. Arnott who has relinquished his position for reasons of health.

Dr. McNall has been with Westinghouse since 1936 in the positions of research engineer and assistant director of research.

Elected by Northwestern Glass

Allen J. Erickson and Gordon W. Roessler have been elected vice presidents of engineering and manufacturing, respectively, at Northwestern Glass Company.

Mr. Erickson has been with the company fourteen years and served as plant engineer prior to his election.

Mr. Roessler, with the company 27 years, was formerly production manager.

Clayton B. Johnson

Clayton B. Johnson, secretary and treasurer of Fairmount Glass Works, Inc. died at his home on May 16th. He was 82 years old.

Mr. Johnson began working at Fairmount in November, 1904, after teaching in the Grant County, Ind., schools for 7 or 8 years.

Many of his interests stemmed from the fact that all his life he was a birthright Quaker. He was a member of the First Friends Church of Indianapolis for over 54 years and was extremely interested in Christian Education and Service on a local, national and international basis. In addition, he was a supporter of the International Council of Religious Education (now the National Council of Churches) and served this organization in an advisory capacity. He also worked continuously with the American Friends Service Committee.

John R. Harkness, president of Fairmount Glass Works, says of Mr. Johnson, "From the human standpoint, he was a very modest man. I don't think he would want a lot of bouquets thrown his way. For steadfastness, loyalty, honesty, directness of approach, accessibility and interest in the people he loved, he had no equal."

Robert L. Warren

Funeral services were held on May 29, for Robert L. Warren, former President and Board Chairman of Brockway Glass Company.

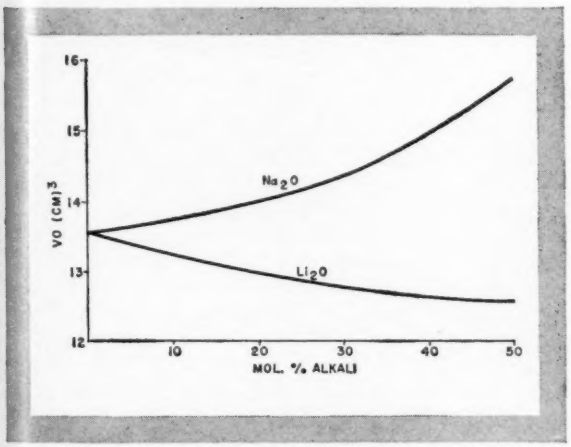
He had been president of Brockway for twenty-one years, during which time the company built new plants in Crenshaw, Pa.; Muskogee, Okla.; Lapel, Ind. and renovated its operations in Brockway, Pa. He held the position of chairman of the board from 1949 to 1954.

Robert L. Warren

In addition to his positions with Brockway, Mr. Warren was active in the Manufacturers Association of Northwest Pennsylvania, of which he was president. He was president and director of the Beadle Corporation; vice president and director of the Pennsylvania Manufacturers' Association; past president of the Glass Container Manufacturers' Institute and director for Home Telephone Co., DuBois Deposit National Bank, St. Louis Car Company and United States Glass Company. He is survived by his wife and three children.

Tightening Glass Networks with the Lithium Ion

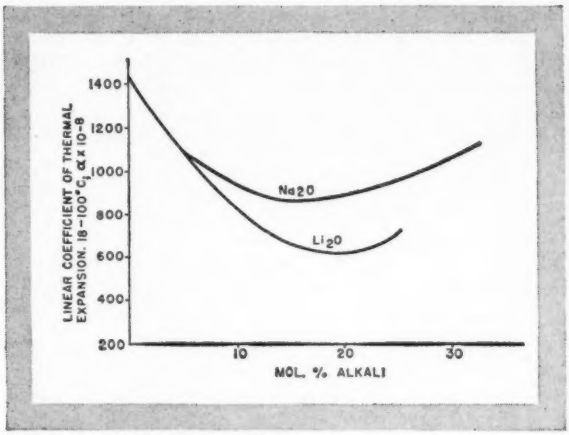
As an alkali is added to silicate glass, density measurements show a steady increase in the volume of glass containing one gram atom of oxygen (Huggins' V_o, Stevel's V). But this progressive loosening of the network does not occur when lithium is added. As can be seen in the accompanying diagram, V_o actually *decreases* with increasing lithium additions, indicating a definite contraction of oxygen ions. For that matter, both eucryptite and spodumene form glasses with higher densities than the equivalent crystalline form.



Effect of Li_2O and Na_2O on V_o of Alkali-Silicate Glasses

By tightly binding alkali ions in the network holes, lithia additions can confer several benefits on glass, ceramic body, and enamel compositions. Among them:

- improved chemical durability
- increased hardness and abrasion resistance
- lower electrical conductivity
- lower thermal expansion



Thermal Expansion of Alkali-Borate Glasses

All of these general properties are not apparent in *all* lithia compositions.

But before the practical extent of such improvements can be forecast with accuracy for a given composition, more information will be needed. As a supplier of lithium chemicals and glass grade lithium minerals to the glass industry, we are doing everything we can to develop it through a continuing exploration of lithium glass forming systems.

The fruits of this research program and our years of practical experience can be brought to bear on your problems. We'll gladly arrange discussions with our engineers. Write Foote Mineral Company, 477 Eighteen West Chelten Building, Philadelphia 44, Pennsylvania.

FOOTE MINERAL COMPANY

INDUSTRIAL LITHIUM CHEMICALS • GLASS GRADE LITHIUM MINERALS (PETALITE, SPODUMENE, LEPIDOLITE, AMBLYGONITE) • FELDSPAR IRON PYRITES • CHROMITE

INVENTIONS AND INVENTORS

Annealing and Tempering

Optical inspection units for bottled goods. Patent No. 2,863,355. Filed March 29, 1955. Issued December 9, 1958. No sheets of drawings; none reproduced. By Harold A. Ledingham and Cornelius E. Smith.

The object of the present invention is to provide a bottle inspection device in which a secondary conveyor is provided with deflecting means adapted to deflect bottles from the main conveyor onto a secondary conveyor and in which the secondary conveyor has a linear foot per minute speed less than that of the main conveyor thereby assuring that the bottles pass the inspection device in bottle to bottle contact. This bottle to bottle contact cuts down the light distortion between the source of light, the bottle to be inspected, and the inspector. If a gap exists between the bottles the inspector is momentarily blinded to inspection for foreign substances in the beverage bottle.

There were 2 claims and the following references cited in this patent.

United States Patents

1,502,692, Sterrett, July 29, 1924; 1,885,892, Bronander, Nov. 1, 1932; and 2,446,377, Marshall, Aug. 3, 1948.

Foreign Patents

635,499, Great Britain, Apr. 12, 1950.

Feeding and Forming

Machine for molding glass articles. Patent No. 2,863,260. Filed October 6, 1954. Issued December 9, 1958. No sheets of drawings; none reproduced. Assigned to Owens-Illinois Glass Company by Walter J. Toepfer and William A. Stutske.

The invention relates to a machine for press molding hollow glass articles. It provides a novel method and means for molding the interior surfaces of the articles.

It comprises an annular series of press molds on a mold carriage and means for rotating the mold carriage intermittently step by step. A plurality of screw threaded inserts, hereinafter referred to as screws, are carried on an annular conveyor which is rotated about the axis of the mold carriage. Means are provided for transferring the screws in succession to a press plunger and operating the latter to mold a charge of glass in the mold with the screw imbedded in the glass.

As the mold carriage rotates step by step each mold with the imbedded screw is brought to a take-out station where the screw is gripped by a chuck. The chuck is then rotated spirally to unthread the screw from the molded article. A transfer arm then returns the screw to a holder on the screw conveyor.

By the use of a plurality or multiplicity of such inserts or screws, their temperature may be controlled and overheating prevented. Cooling means such as air blowers may be used for applying cooling air to the screws on the screw conveyor. Burners may also be arranged for applying heat to the screws where required to control or vary the temperature of the screws.

There were 8 claims and the following references cited in this patent.

United States Patents

998,673, Burleigh, July 25, 1911; 1,049,594, Olsen, Jan. 7, 1913; 1,522,150, Smith et al., Jan. 6, 1925; 1,642,658, Holmes, Sept. 13, 1927; 2,146,346, Nelson, Feb. 7, 1939; and 2,331,053, Shillinger, Oct. 5, 1943.

Furnaces

Flow spout construction. Patent No. 2,838,880. Filed January 2, 1957. Issued June 17, 1958. No sheets of drawings; none reproduced. Assigned to Libbey-Owens-Ford Glass Company by Alfred H. Bailey and John C. Blaine.

The present invention relates broadly to continuous melting furnaces and, more particularly, is concerned with an improved outlet or flow spout for such furnaces.

An object of the invention is to provide an improved shoulder and edger block mounting structure whereby both blocks can be shifted substantially as an integral unit to vary the width of a glass ribbon prior to being formed.

By employing the improved flow spout construction, adjustment in the width of formed glass ribbon can be more rapidly carried out by moving the shoulder blocks with the assurance that the cooperating edger blocks will be maintained in their established positions without time-consuming readjustment. Also, since suitable adjusting means are provided, initial and minor adjustment of the edger blocks can be effected to obtain their accurate position both with respect to the shoulder-blocks as well as the forming rolls.

There were 7 claims and the following references cited in this patent.

United States Patents

1,735,595, Blair, Nov. 12, 1929 and 1,859,862, Boudin, May 24, 1932.

Glass Compositions

Optical crown glass. Patent No. 2,866,712. Filed November 16, 1953. Issued December 30, 1958. No sheets of drawings; none reproduced. By Gustav Weissenberg and Otto Ungemach and Norbert Meinert.

Glasses with anomalous dispersions are especially valuable to the optical computer because with them it is possible to correct the secondary spectrum by means of a lens system.

It has been found that optical glasses of high values with the desired negative $\triangle v$ values can be obtained by melting down a mixture of boric acid anhydride and zirconium oxide in the presence of a carbonate of an alkali metal (preferably of lithium or sodium or both) or a mixture of boric acid anhydride, a metaborate of an element of the second group of the periodic system, zirconium oxide and lanthanum oxide.

The glass melts of the invention are illustrated in the following table:

In per cent by weight

Melt No	Ko 387	Ko 393	Ko 395	Ko 397	Ko 398
B_2O_3	24.8	22.9	22.9	26.0	25.0
$CaOB_2O_3$	14.9	13.8	13.8	15.7	15.0
La_2O_3	39.7	45.7	45.7	41.6	40.0
ZrO_2	15.8	16.6	16.6	8.35	10.0
PbO	4.8	.....	.....	.....	.....
Al_2O_3	.....	1.0	.....	.....	.....
BaO	.....	.....	1.0	.....	.....
Nb_2O_5	.....	.....	.....	8.35	.....
Ta_2O_5	.....	.....	.....	.....	10.0
n_D	1.7739	1.7860	1.7857	1.7669	1.7614
v (nu)	46.2	47.2	47.2	44.7	47.2
[illegible]	p	q	r	s	t
ξ	0.559	0.552	0.553	0.555	0.553
$\triangle v$ (nu)	−3.9	−7.1	−6.5	−7.8	−6.5

There were 3 claims and the following references cited in this patent.

United States Patents

2,678,281, Geffcken et al., May 11, 1954.

Other References

De Paolis Abstract 700156, published December 6, 1949.

Glass Wool and Fiber

Apparatus for manufacture of fibers of inorganic thermoplastic material. Patent No. 2,814,828. Filed March 26, 1954. Issued December 3, 1957. No sheets of drawings; none reproduced. Assigned to Hoganas-Billesholms by Ake Karl Erik Svende.

This invention relates to an apparatus for the manufacture of inorganic fibers, particularly of glass, slag or other thermoplastic, inorganic material, in which a jet of the melted, fluid material is transformed into fine threads by the centrifugal effect of a rotating disk.

The method is based upon the use of a rotating centrifugal disk, is mainly characterized in that the fibers thrown out from the disk, immediately after having left the edge of the disk, are exposed to the action of a first stream of air, directed downwards at an angle to the vertical, so as to form staple fibers, and preferably somewhat later are exposed to the action of a second stream of air, directed more horizontally, whereafter the fibers, if desired, are coated with a liquid binder or lubricant. The binder or lubricant to be added is preferably dispersed in the horizontal stream of air, said stream of air thus transporting the binder or lubricant to the fibers.

The apparatus consists substantially of a centrifugal disk apparatus, and is mainly characterized in a blowing fan impeller being provided upon the same shaft as the centrifugal disk, and under said disk, the blowing fan impeller consisting of two conical funnels partly pushed over each other, fan blades being provided in the interstice between the two funnels so as to produce the first stream of air which is directed downwards at an angle to the vertical. The lower funnel is preferably at its lower edge provided with a circular flange, turned outwards and being provided with fan blades underneath, so as to produce the second, horizontally directed stream of air, which among other things shall prevent the fibers from sticking to the bottom of the mantle surrounding the impeller.

A uniform stream of a staple fiber product having very good qualities for the manufacture of felt and plates is produced in the apparatus.

There were 3 claims and the following references cited in this patent.

United States Patents

884,571, Cowing, Apr. 14, 1908; 2,136,988, White, Nov. 15, 1938; 2,255,227, Parsons, Sept. 9, 1941; 2,328,714, Drill et al., Sept. 7, 1943; and 2,707,847, Anliker, May 10, 1955.

Foreign Patents

143,472, Australia, Sept. 18, 1951; 147,892, Australia, Aug. 22, 1952; and 668,490, Great Britain, Mar. 19, 1952.

Miscellaneous Processes

Apparatus and method for silvering mirrors. Patent No. 2,815,298. Filed April 6, 1953. Issued December 3, 1957. Two sheets of drawings; none reproduced. Assigned to The Toledo Plate & Window Glass Company by Howard H. Heffley.

According to the invention the glass to be silvered is carried on a conveyor through a preparation zone, a silvering zone, and finishing zone. In the silvering zone a plurality of pairs of nozzles are carried on a framework for reciprocation transversely of the conveyor. One nozzle of each pair is supplied with silver solution while the other nozzle supplies the reducing solution. The discharge from the nozzles, in fan shaped streams, impinges on the glass in a generally elliptical mixing zone where the two solutions are thoroughly mixed and from which zone the solution flows in all directions on the surface of the glass.

As the framework carrying the nozzles reciprocates across the sheet of glass on the conveyor the streams from the nozzles provide areas of fresh solution, one area for each set of nozzles, separated by intermediate areas of spent solution or sludge. Since the nozzles follow a fixed transverse path while the glass is moving slowly along the conveyor this area of fresh solution extending across beneath the nozzles moves across the face of the sheet of glass. Similarly, the spent solution or sludge held between the paths of the nozzles also moves relative to the glass and finally drains down through the conveyor as the trailing edge of the glass sheet passes the path of the nozzles.

There were 5 claims and the following references cited in this patent.

United States Patents

1,919,798, MacLaurin, July 25, 1933; 2,118,212, MacLaurin, May 24, 1938; 2,505,179, Gaythwaite, Apr. 25, 1950; and 2,581,957, Jones, Jan. 8, 1952.

Research Digest

Surface Tension and Density Measurements on Molten Glasses

• THE WORK DESCRIBED by L. R. Barrett and A. G. Thomas in the *Journal of the Society of Glass Technology*, April 1959, was undertaken as part of a program of research into the physical and chemical factors influencing the attack of refractories by slags. The phenomena associated with surface tension are of considerable importance because of the part they play in wetting by molten slags. Values for the densities of slags at high temperatures are necessary for the evaluation of diffusion coefficients.

In addition, the changes in surface tension and density which take place when the temperature or composition is altered, reflect the accompanying changes in the structure of molten silicates; a study of these changes assists in building up a model of the molten state of these silicates, and leads to a better understanding of chemical processes in which they are involved.

Many workers have investigated the surface tension of molten glasses using the maximum bubble pressure method. A description of a typical apparatus has been given by Parmalee, Lyon & Harmon. Such an apparatus consists essentially of a means for blowing bubbles of gas at the end of a capillary tube immersed in the liquid under investigation, and simultaneously measuring the pressure attained in the bubble.

The principal difference between the present apparatus and that described previously is that a device for measuring the depth of immersion of the capillary tube in the glass has been added.

The capillary tube was constructed from an alloy of 10 per cent rhodium and 90 per cent platinum, with an internal diameter of 0.25 cm at the tip. The glass under investigation was contained in a platinum crucible with a capacity of 100 cc., and the furnace was wound with molybdenum tape. The pressure measurement was carried out by observing the movement of liquid in a manometer by means of a travelling microscope. The procedures for drying the gas, adjusting the pressure, lagging to prevent temperature fluctuations and aligning the capillary tube were similar to those described by Parmelee, Lyon & Harman.

After the temperature of the melt had been raised to a suitable value and sufficient time had elapsed to ensure homogeneity of the melt, measurements were commenced.

The capillary tube was lowered into the crucible until it was located at the surface of the melt. The method of finding this position has also been described previously as has the method of ascertaining the maximum bubble pressure at this point. The capillary tube was next lowered an arbitrary amount and the maximum bubble pressure again determined.

This measurement was again repeated after lowering the capillary tube a further known distance. Distances of 0.100, 0.200, 0.300, and 0.400 in. were used, the larger values being preferred. The density of the melt can be calculated easily from an equation.

Measurements of surface tension and density carried out on a number of liquids at room temperature indicated the order of accuracy which could be expected from the method. The additional difficulties involved in dealing with molten glasses increased the errors and the estimated error in density is ± 2 per cent over the practicable range of viscosities, that is, less than 10-15 poises. Surface tension measurements on the other hand could be made with melts having viscosities of several hundred poises. The limiting factor in the case of the density was the lengthy period which would have to elapse before the achievement of stable conditions prior to each reading.

Examination of the results reveals certain general trends in surface tension and density:

1. A linear relationship exsists between surface tension-temperature and—composition and density-temperature and—composition. In particular it should be noted that no discontinuities corresponding to 'compound' formation occur in the composition relationships.

2. The surface tension increases with increasing alumina or decreasing silica content while its temperature coefficient increases with both increasing alumina and silica.

3. The density increases with increasing alumina or decreasing silica while its temperature coefficient increases with decreasing alumina or increasing silica.

4. The temperature coefficients of surface tension are positive for all the compositions studied. Similar behaviour has been reported in other systems by various workers. The system lime-alumina-silica has been little studied. King has examined the surface tension of two compositions. The corresponding values extrapolated from the present work are approximately 5 per cent higher.

His findings on the effect of composition are the same as those of the present work. The results of Ermolaeva are also in agreement with the present work at a temperature of 1600°C, but below this the reported effects of composition on surface tension are different. The numerical values for surface tension reported by Ermolaeva are 25-50 per cent lower than those obtained in this work.

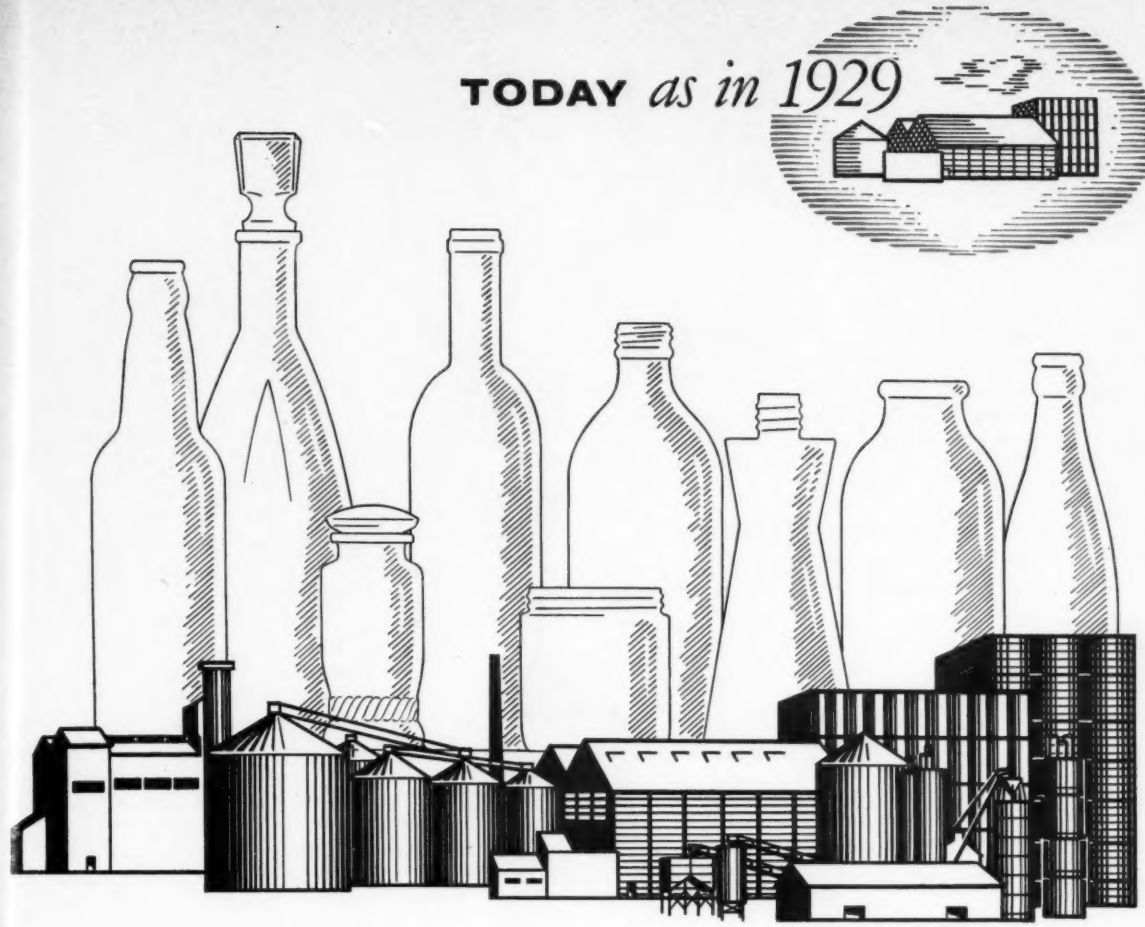
No observation of densities in the three component system have been noted in the literature.

In such complex systems as molten silicates of three or more components it is difficult to interpret the results of measurements of physical properties in terms of structure. The results of the present research enable certain broad conclusions to be drawn, however.

The most significant fact to emerge is that the variation of the measured physical properties with composi-

(*Continued on page* 397)

TODAY *as in 1929*



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CURRENT STATISTICAL POSITION OF GLASS

Employment and payrolls: Employment in the glass industry during April, 1959, was as follows: *Flat Glass*: a preliminary figure of 29,700 for April, 1959, indicates an increase of 0.33 per cent under the adjusted figure of 29,800 reported for March, 1959. *Glass and Glassware, Pressed and Blown*: an increase of 1.9 per cent is shown by the preliminary figure of 83,800 reported for April, 1959, when compared with the adjusted figure of 82,200 reported for March, 1959. *Glass Products Made of Purchased Glass*: the preliminary figure of 14,800 given for April, 1959, is a decrease of 2.6 per cent under the 15,200 reported for March, 1959.

Payrolls in the glass industry during April, 1959, were as follows: *Flat Glass*: a decrease of 0.6 per cent is shown in the preliminary $17,024,413 given for April, 1959, when compared with March's* adjusted $17,134,675. *Glass and Glassware, Pressed and Blown*: An increase of 1.4 per cent is shown in the preliminary $32,243,759 reported for April, 1959, when compared with the previous month's* adjusted $31,784,842. *Glass Products Made of Purchased Glass*: a preliminary figure of $4,755,120 was reported for April, 1959. This is an increase of 0.1 per cent when compared with the adjusted figure of $4,748,621 for March*, 1959.

*Note: Payroll figures reported in this column last month were in error and should be corrected according to the report above.

GLASS CONTAINER SHIPMENTS

(All Figures in Gross)

Narrow Neck Containers

	May, 1959
Food	1,301,000
Medicinal and Health Supplies	1,283,000
Chemical, Household and Industrial	948,000
Toiletries and Cosmetics	895,000
Beverage, Returnable	1,232,000
Beverage, Non-returnable	146,000
Beer, Returnable	707,000
Beer, Non-returnable	963,000
Liquor	855,000
Wine	383,000
Sub Total (Narrow)	8,713,000

Wide Mouth Containers

Food	*3,525,000
Medicinal and Health Supplies	372,000
Chemical, Household and Industrial	153,000
Toiletries and Cosmetics	288,000
Packers' Tumblers	22,000
Dairy Products	140,000
Sub-total (Wide)	4,500,000
Total Domestic	13,213,000
Export Shipments	213,000
TOTAL SHIPMENTS	13,426,000

*This figure includes Fruit Jars and Jelly Glasses.

GLASS CONTAINER PRODUCTION AND INVENTORY

(All Figures in Gross)

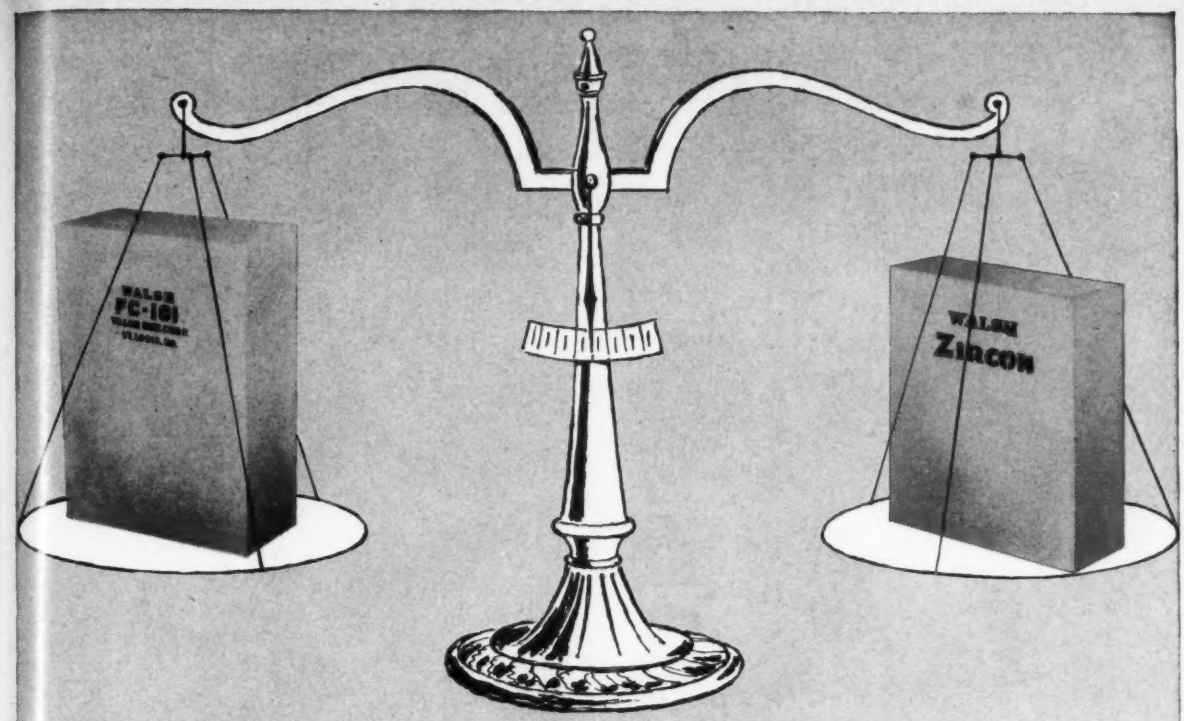
		Production May 1959	Stocks May 1959
Food, Medicinal and Health Supplies; Chemical, Household and Industrial; Toiletries and Cosmetics	Narrow Neck	4,616,000	12,530,000
	Wide Mouth	4,520,000	7,302,000
Beverage, Returnable		1,189,000	2,123,000
Beverage, Non-Returnable		153,000	217,000
Beer, Returnable		582,000	483,000
Beer, Non-returnable		887,000	909,000
Liquor		812,000	1,271,000
Wine		396,000	776,000
Packer's Tumblers		24,000	98,000
Dairy Products		151,000	346,000
TOTAL		13,330,000	19,832,000

*This figure includes Fruit Jars and Jelly Glasses.

Glass Container production: production based on figures released by the Bureau of the Census, Industry Division, was 13,330,000 gross during May, 1959. This is an increase of 0.79 per cent over the previous month's production figure of 13,266,000 gross. During May, 1958, glass container production was 12,159,000 gross, or 9.6 per cent under the May, 1959, figure. At the end of the first five months of 1959, glass container manufacturers have produced a preliminary total of 61,994,000 gross. This is 7.1 per cent more than the 57,884,000 gross produced during the same period in 1958.

Glass container shipments: Shipments of glass containers during May, 1959, came to 13,426,000 gross, an increase of 6.5 per cent over April, 1959. Shipments during May, 1958, amounted to 12,438,000 gross, or 7.9 per cent less than May, 1959. At the end of the first five months of 1959, shipments have reached a preliminary total of 59,876,000 gross, which is 6.5 per cent more than the 56,210,000 gross shipped during the same period the previous year.

Stocks on hand at the end of May, 1959, came to 19,832,000 gross. This is 0.6 per cent less than the 19,943,000 gross on hand at the end of April, 1959, and 5.8 per cent more than the 18,741,000 gross on hand at the end of May, 1958.



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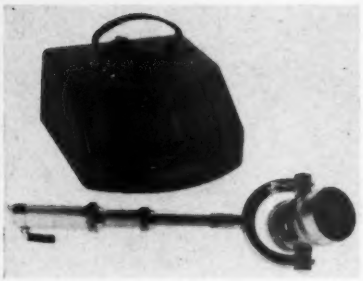


GP Glass Pyrometer

Atlantic Pyrometers, Inc., Hawthorne, N. J., has a GP glass pyrometer said to be the first instrument to measure accurately and simply the temperature of open glass surfaces.

The glass pyrometer reads the temperature of the front surface of hot glass objects only. It has, the company states, an accuracy within one per cent for clear, opaque or colored glasses and requires no external power supply.

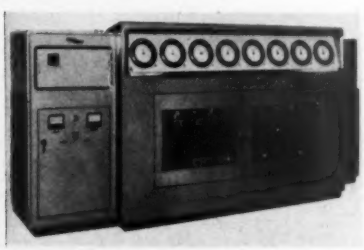
Battery Chart

Exide Industrial Division of the Electric Storage Battery Co., Philadelphia, Pa., has developed a chart which provides a simple method of determining the proper charge rate for any lead-acid motive power battery being charged by motor-generator equipment on an 8 hour basis.

The chart can be used on electric industrial trucks with either shunt-wound or compound-wound generator charger equipment. This applies to lead-acid batteries of any number or size of cells.

Spectrometer

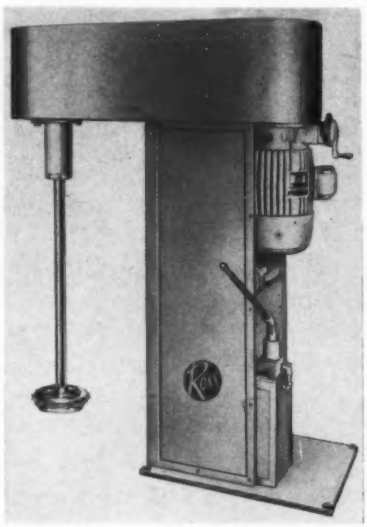
Baird-Atomic, Inc., Cambridge, Mass., has re-engineered and improved the B/A model spectromet permitting a greater number of elements to be analyzed at one time. The chemical composition of metal samples can be determined in less than one minute with the results presented directly in per cent concentration on indicator dials.



High-Speed Dissolver

Charles Ross & Son Co., Brooklyn, N. Y. has developed a new high-speed dissolver or disperser with a specially designed multiple action impeller or millhead which effectively mixes, disperses, dissolves, emulsifies and deagglomerates most types of liquid, paste or heavy paste materials.

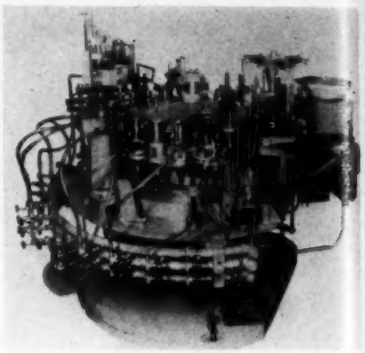
Available in laboratory or very large production sizes the disperser can be used in any size tanks or containers



from standard 55-gallon steel drums up to tanks measuring 40″ diameter by 45″ deep. Millhead speeds can be set anywhere between 2059 FPM and 10323 FPM.

Alumina Plastic Refractory

H. K. Porter Co., Inc., Pittsburgh, Pa., has developed a new 80 per cent alumina plastic refractory, "Pitco 80" which is said to combine all advantages of monolithic construction, formerly available only in castables and ramming mixes. It has the advantages of plastic construction: air and gas tight, no special shapes needed, high thermal shock resistance, and withstands heavy loads and temperature variations.



Button Stem Machine

Kahle Engineering Co., Union City, N. J., has designed an automatic button stem machine that produces 1000 non-tubulated miniature and subminiature electronic tube stems per hour.

The new machine has 24 heads with two upper molds for making non-tubulated stems with short lead wires. The company also offers another machine that produces tubulated stems or stems with long lead wires such as those used in cathode ray tubes.

The unit has dual-motor drive, one for the heads, the other for indexing and cam mechanism, both independent of one another; optional automatic wire feed and glass feed; automatic unloader; readily removable individual head units; two press positions and one puddle, and harmonious barrel cam and roller index. The machine weighs 4000 lbs., is 5′9″ high and has a diameter of 5′6″.

CATALOGS RECEIVED

Specific gravity indicators. (2 pages) Describes instrument for continuous measurement of liquid specific gravity; includes construction details, plus dimensional and cross-sectional drawings.

SCHUTTE AND KOERTING CO., Cornwells Heights, Pa.

Instrument and control panels. (16 pages) Details of construction, dimensions, weights, instrument mounting and accessories for six standard styles. Includes standard procedures for tubing and wiring.

BAILEY METER CO., Cleveland, Ohio

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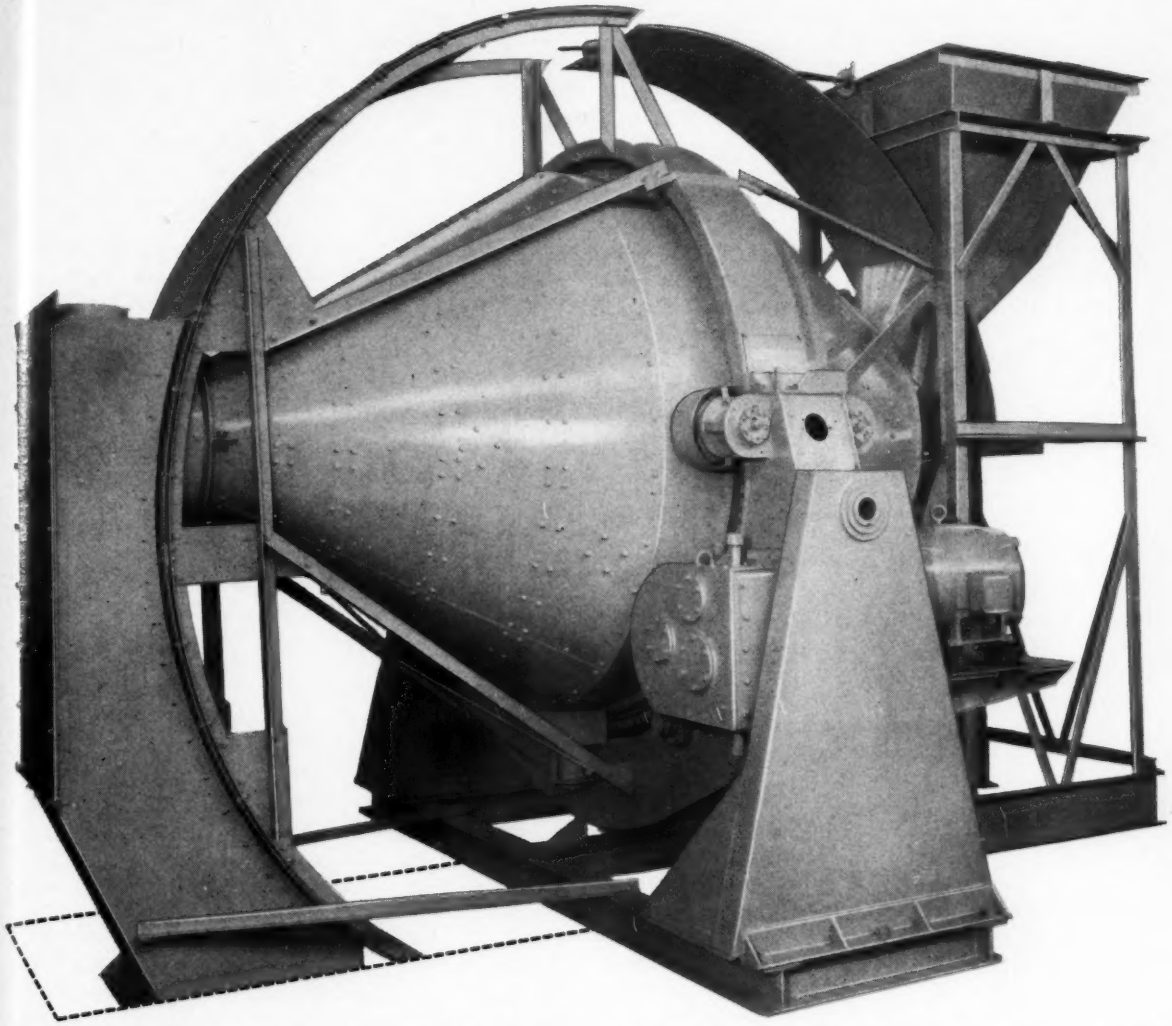

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NEW BOOKS

Handbook of Chemistry and Physics (40th Edition, 1958-1959) Chemical Rubber Publishing Co., Cleveland, Ohio; 3,456 pages; $12. (Outside U.S.A. add 50 cents).

In order to keep this Handbook as up to date as possible the editors have added fourteen new tables to this latest edition, among which are: Physical Constants of the Rare Earth Compounds; Thermodynamic Properties of the Oxides; Moisture Content Values; Ion Exchange Resins; Superconducting Transition Temperatures; and Electron Physics Table.

A special section of 531 pages contains General Chemical Tables providing such information as Flame and Bead Tests; Approximate pH Values; Polarographic Analysis; Dissociation Constants; Gravimetric Factors; and Isothermal Compressibility of Liquids.

The Chemistry and Physics of Clays and other Ceramic Materials, *by Alfred B. Searle and R. W. Grimshaw* (Third Edition, entirely revised and enlarged; 1959). Interscience Publishers, New York; 942 pages; $16.25.

The 14 main chapters deal with the nature of ceramic materials and clays, including their atomic and crystalline structure. Detailed methods of identifying and estimating ceramic materials are described, such as spectrographic, chromatographic and X-ray analyses; electron diffraction, infra-red, and microscopic examination and analysis. Other phases of study include chemical and mineralogical composition, physical and structural properties, the influence of water in ceramic systems; equilibrium state and physico-chemical reactions; chemical and physical changes in ceramic materials; and strength and allied properties.

This book has been compiled to cover the requirements of students of ceramics to full degree level in both Great Britain and the United States.

Rare Metals Handbook, *edited by Clifford A. Mampel,* Consultant (Third Printing, 1959). Rheinhold Publishing Co., New York. 657 pages; $12.

The full range of available data on more than 35 less-common metallic elements. Information about each element is arranged for convenient reference to such important subjects as occurrence, production, statistics, economics, derivation, physical and chemical properties, fabrication, techniques, and present and potential uses.

Properties and comparisons between metals are shown in tabular form wherever possible; complete reference lists close each chapter.

Among metals discussed are: beryllium, boron, cadmium, barium, strontium, cobalt, gallium, germanium, lithium, molybdenum, platinum, selenium, silicon, tellurium, thorium, tungsten, uranium and zirconium.

Journal of Glass Studies, *The Corning Museum of Glass* (Volume 1, 1959). 135 pages; $5. (Outside U.S.A. add 50 cents).

This scholarly volume has been published with the purpose of helping to record the art and history of glassmaking. The editors plan to publish one such volume each year. Contents of the present work include an article on Glass Manufacture in Ancient Crete; a 12th Century Scent-Bottle from Cyprus; Ancient Glass of Japan; An Amelung Sugar Bowl; A Pair of 19th Century American Tankards with Japanese Coins.

At the end of the volume is a check list of recently published articles and books in glass from 1956 through 1958 which will be expanded in successive publications.

This first volume is well illustrated and has extensive references to the original literature.

Books Recently Reviewed

Surface Chemistry. Theory and Application, *by J. J. Bikerman,* Massachusetts Institute of Technology, (Second Edition, revised and enlarged, 1958). Academic Press, N.Y. 501 pages; 160 figures; $15.

Many properties of glass are referred to—strength of glass filaments; surface tension of molten glass; absorptive capacity of glasses. Contains a great deal of information of interest to the glass technologist.

Dislocations and Mechanical Properties of Crystals *(edited by J. C. Fisher, W. G. Johnston, R. Thomson and T. Vreeland, Jr.).* John Wiley & Sons, N.Y. 634 pages; $15.

A symposium volume incorporating the knowledge of 54 authorities. An outstanding feature is the coverage of principal methods for observing individual dislocations. The more complicated and least understood areas in the field are reviewed, including such topics as work hardening, recovery, dislocation, damping and fatigue.

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Glass Bubble Canopy

(*Continued from page* 358)

sary precision so that they could later be joined with a plastic interlayer. Laminated plastic canopies are, of course, formed employing the same tooling and techniques used for making monolithic canopies. On the other hand, glass laminates cannot be post-formed since no plastic material is sufficiently stable to withstand the temperatures necessary for shaping laminates to bubble canopy configurations.

To be successful as a transparent roof enclosure, a glass bubble canopy would have to be made with annealed glass and adequate strength built into it by employing heavy plastic interlayers and greater glass thicknesses than now normally employed. Increase in glass and plastic thicknesses bring a weight penalty, not to mention cost factors.

Weather-Tight Mounting

Assuming that a successful technique for forming and laminating a glass canopy were developed, one then encounters the problem of weather-tight mounting such a canopy on the automobile. While the mounting problem undoubtedly can be solved, it can only be done by additional expense, such as resorting to the use of metal inserts around the periphery, or floating the canopy in non-rigid mountings. To successfully mount an all-glass canopy, the wide difference in coefficient of expansion of glass and metal must be considered and the problems arising therefrom overcome.

Optical Problems

In forming a glass bubble canopy by any presently visualized method, thinning of the glass during forming would inevitably result. This introduces immediate optical problems which must be overcome. The adoption of curved glass by the automotive industry has been cautious, and great care taken to guarantee good vision,[1, 2] not only to the driver but to other occupants of the vehicle as well. A multiplicity of optical problems automatically arises from the use of a glass bubble canopy, the degree of the severity of the problem, of course, dependent upon the particular contour or geometry of any specific design.

Solar radiation

The adoption of an all-glass bubble canopy for automobile glazing will also multiply problems now encountered as the result of expanded glass area usage in present production models. Even when automobiles are air-conditioned, occupants could be decidedly uncomfortable due to the large influx of solar radiation through a canopy-type glazing.

Solar energy[3, 4] is broadly comprised of three components: ultraviolet, visible, and infra-red radiation. Three per cent of the total solar energy is contained in the ultraviolet region, 45 per cent in the visible region, and 52 per cent in the infra-red. Neither the ultraviolet nor the infra-red is, of course, useful for vision purposes. It should be recognized that the 45 per cent of total solar energy present in the visible region, although useful for seeing, will heat the occupant or interior of a vehicle if absorbed.

The A. S. A. Code now requires that glazing materials in areas requisite for driving visibility transmit at least 70 per cent of the visible light[5, 6]. This means that (assuming all of this visible light is absorbed) about 30 per cent of the total solar radiation must enter the vehicle in requisite vision areas and can be converted into heat by absorption.

To insure greater passenger comfort and the safety that goes with it, automobile manufacturers have adopted the use of heat-absorbing glazings having nominal transmittances of about 70 per cent as contrasted with standard glasses of the non-heat-absorbing type which transmit about 90 per cent of visible radiation. The use of such heat-absorbing glazings for automobiles with their resultant 20 per cent decrease in visible transmittance has led to controversy and a number of papers have been published questioning use of glass of the heat-absorbing type[7, 8, 9, 10].

Actually when all such publications have been analyzed, it would appear that the most factual findings are those detailed in papers written by Doane and Rassweiler[11] and by Roper[12]. These studies show that the use of heat-absorbing glazings having visible transmittances of about 70 per cent have little, if any, effect on one's ability to see adequately during the daytime and only a minor, and insignificant, effect on threshold vision when driving at night.

Ideally, a glazing material would prevent all but 30 per cent of the solar radiation from entering the passenger compartment of an automobile. A number of ways of accomplishing this, in some measure at least, are to (1) absorb the radiation, (2) reflect the radiation from the glazing surface, or (3) combinations of both.

Of the two methods of rejecting solar radiation, the reflection method appears superior since, when solar radiation is absorbed by a glazing material, it increases the temperature of the glazing material, resulting in reradiation to the vehicle interior. By reflecting the radiation, one prevents it from entering the passenger compartment and minimizes the heating effects. It is to be hoped that a film can be produced which could be applied to the outside surface of the automotive glazing and selectively reflect the infra-red and ultraviolet portions but not reflect too much light in the visible region. A filmed glazing which reflects 20 or 30 per cent of visible light could be extremely annoying and possibly hazardous to motor vehicle operators encountering such mirror-like glazings on the highway when the sun is oriented in certain positions.

At the present time, heat rejection from automobiles by glazing materials is being accomplished in three ways:

(1) The use of heat-absorbing glass which absorbs approximately 50 per cent of the total solar radiation, some in the ultraviolet, some in the visible, but the majority in the infra-red.

(2) In areas not requisite for driving visibility, the solar radiation load is cut down by use of shaded areas in combination with heat-absorbing glass, the shading being accomplished by dyeing the plastic interlayer of a laminated glass. If the visible transmittance of the shaded area averages 5 per cent, this means that almost

43 per cent of the visible light which might otherwise be absorbed by the car occupant's clothing or the car interior is prevented from entering the vehicle. Shaded areas also assist in cutting out some of the ultraviolet but few dyestuffs absorb very much infra-red radiation.

(3) Films applied to glass are being used, and these reflect substantial portions of the ultraviolet, visible, and infra-red radiation while at the same time absorbing as much as 70 or 75 per cent of the visible light. These films, up till now of course, have only been employed where the 70 per cent requirement of visible light transmittance does not apply.

In closing these remarks, it is quite evident that before glass bubble canopies can be entertained seriously for glazing production automobiles, a number of obstacles must be overcome. The use of such glazings, even if perfected, poses problems of access and egress from vehicles; whether or not average car buyers will accept such designs only time alone will tell.

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Glass Division Papers

(*Continued from page* 355)

Tuesday Morning

Symposium on Behavior of Glass in the Viscoelastic Range began on Tuesday morning. The session was guided by H. R. Lillie as chairman.

VISCOELASTIC BEHAVIOR OF SOLIDS, by E. R. Fitzgerald, Department of Physics, The Pennsylvania State University.

Mr. Fitzgerald first considered the principles involved when various viscoelastic solids were stressed. The behavior was illustrated by mechanical models, and more complex phenomena were derived from these simple illustrations.

The response of a solid to an applied stress is in general partly elastic and partly viscous. That is, a recoverable deformation occurs along with a permanent deformation or flow. If the stress is time-dependent, the elastic part of the deformation is instantaneous or entirely in phase with the stress while the viscous part of the response may be considerably delayed and hence out of phase with the applied stress. Thus if a solid is subjected to an applied stress varying sinusoidally with time, the resulting strain is sinusoidal but has one component in phase with the stress and another component 90° out of phase.

The relative proportion of strain in each phase cannot in general be predicted from the static mechanical properties of the material, and, therefore, the dynamic characteristics are of importance in the design and operation of devices which are likely to be subjected to vibration or other dynamic stresses. At the same time the dynamic response of a material reflects various molecular processes and motions which occur in the solid state and is of considerable value in attempts to gain increased understanding of molecular structures and inter-molecular forces.

Representative data were cited showing the dynamic characteristics of various materials including metals, single crystals of sodium chloride, copper sulfate, and quartz, fused quartz and amorphous and crystalline polymers. Variations of dynamic mechanical properties with frequency and temperature were discussed, together with brief references to the particular mechanisms believed to be responsible for the behavior observed in each case.

In summarizing, Mr. Fitzgerald pointed out the characteristics of elastic solids, viscous liquids, Maxwell solids, Kelvin solids, and combinations of Maxwell and Kelvin solids.

VISCOELASTIC BEHAVIOR OF HIGH POLYMERS, by Hersel Markovitz, John Hopkins University, Baltimore, Maryland.

The static elasticity of some high polymers undergoes a transition from a rubber-like modulus (about 10^7 dyne/cm.^{2}) to glass-like modulus (about 10^{10} dyne/cm.^{2}) as the temperature is lowered through a narrow transition region. A similar rise in the dynamic modulus occurs at constant temperature as the frequency of the sinusoidal deformation increases. Similar effects were also observed in other time-dependent experiments; e. g., creep and stress relaxation. Thus these viscoelastic properties are interrelated. For all of these properties there is a single time-temperature relationship in the region which, furthermore, has the same form for a large variety of materials and which contains essentially one parameter, the glass transistion temperation. The viscoelastic properties in the glassy and rubbery regions were also included, and the effect of molecular structure and parameters was discussed.

Mr. Markovitz attempted to show the viscoelastic characteristics of organic polymers of high molecular weights and the vast importance of the transitions occurring in such materials. The viscoelastic properties of such materials were said to be greatly influenced by amorphous or crystalline character, cross-linkage, glassy or rubbery character, copolymer or hompolymer structure, oriented character, molecular weight, diluent present, and whether or not fillers had been added.

DEFORMATION OF GLASS UNDER CHANGING LOADS, by Franklin F. Y. Wang, Ceramic Research Laboratory, A. O. Smith Corporation, Milwaukee, Wisconsin.

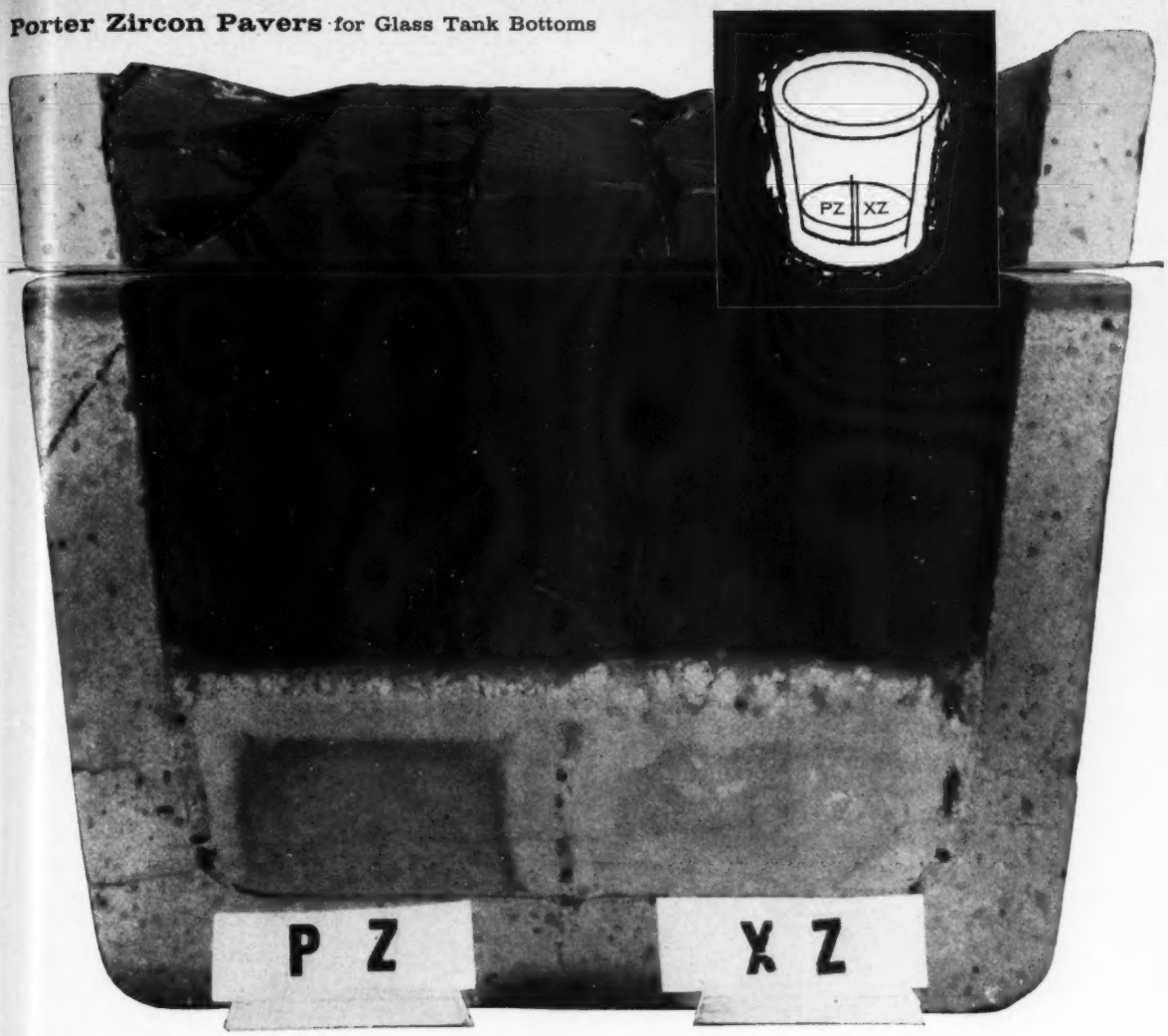
The viscoelastic behaviors of a glass, subjected to a linearly changing load (i. e., $P = P_o + at$), were studied at constant temperatures. The results were analyzed with the aid of the Voigt model of springs and dashpots. Viscoelastic parameters of the glass were determined from the data, and the effect of stress on these viscoelastic parameters was discussed.

Details of the test involving fiber-elongation methods was explained along with certain assumptions which were made.

Glass may be considered as a truly viscoelastic material. The mechanical model of Voigt was decidedly

(*Continued on page* 386)

Porter Zircon Pavers for Glass Tank Bottoms



Torture test proves Porter Zircon Paver

This unretouched photograph shows comparison of Porter PZ Zircon and another commercially made Zircon Paver, after an extensive glass corrosion test. The sketch and photograph illustrate a 6″ diameter crucible with two semi-circular test pieces 1″ thick, cut and cemented with Zircon Cement to form a paved bottom. Crucible was held at 2680°F for 24 hours, filled with molten soda-lime container glass. Crucible was then cut in half across center of both test pieces to show comparison. Crucible partly immersed in liquid of same refractive index as glass to eliminate effects of saw marks and fracturing of glass and to give clear view of glass directly above and in contact with test pieces.

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(*Continued from page* 384)
useful in reducing the variables in the random characteristics of a glass when determining the viscoelastic character of the glass.

A method was described for measuring the stress birefringence properties of soda-lime glasses in the range 23° to 650°C. Data on three glasses showed that the stress-optical coefficient increases slowly with temperature, reaching a definite maximum in the range 570° to 590°C. The same apparatus was used to measure the rate of stress release in two of these glasses. Data obtained under thermal equilibrium conditions may be represented by equations that suggested that two or more concurrent mechanisms were involved in the stress release in these glasses within the viscosity range log 12 to log 14.5 (a rapid one of 0.4 to 10 minutes in duration and slow one of 2 to 60 minutes).

RATE OF STRESS IN VISCOELASTIC RANGE, by D. A. McGraw, Owens-Illinois Technical Center, Toledo, Ohio.

Data were presented on the stress-optical coefficients and rates of stress release in soda-lime, potash-barium, and borosilicate glass compositions in their respective annealing ranges. The results indicated that both viscous flow and delayed elastic return were involved in the release of stress. The rate of stress release was further dependent upon the existing stress, increasing as the stress magnitude was raised.

Stress was relieved principally by viscous flow at temperatures near log viscosity = 13. Here the rate was inversely proportional to viscosity and directly proportional to stress. At higher viscosities the initial stress was relieved faster than indicated by an inverse viscosity relation. In this region an appreciable part of the stress release was achieved by delayed elastic return.

The release of stress in each glass type may be represented by a relation that implies at least two rate processes. The specific roles of the three variables, viscosity, delayed elasticity, and stress magnitude, appeared to vary with composition.

Tuesday Afternoon

INTERNAL FRICTION OF GLASS IN THE TRANSFORMATION RANGE, by L. E. Ashman and Neill M. Brandt, Mellon Institute, Pittsburgh.

The paper was presented by Mr. Ashman. Details of the apparatus and furnace used to measure the internal friction in soda-silica glass rods at temperatures between 400°C. and 600°C. were given. The frequencies used varied from 10^{-4} cycles/sec. to 1 cycle/sec.

Results of measurements on a simple sodium silicate glass showed marked changes in its internal friction spectrum at temperatures between 450°C. to 500°C. Beyond 500°C. the glass behaved as an ideal Maxwell Solid. The glasses used were similar to those used by Taylor a number of years ago. The results indicated an excellent confirmation of his ideas on the decay in glass.

RELATION OF PHOTELASTIC AND VISCOELASTICS BEHAVIOR, by Harold T. Smyth, School of Ceramics, Rutgers, The State University, New Brunswick, New Jersey.

Mr. Smyth attempted to explain the photoelastic and viscoelastic behavior in glass in terms of a network model rather than a mechanical model of dashpots or similar illustrations.

It was shown that some glasses, when chilled from temperatures in the annealing range under load developed a permanent birefringence when the load was removed at room temperature. When the same glasses were chilled from temperatures slightly higher, the birefringence became too small to measure. In explaining this phenomena, the author assumed that the permanent birefringence arose because there existed in the glass a non-random directional distribution of Si—O—Si links caused by the preferential breaking of those most closely aligned with the applied tension. It has been shown by the author that the attainment of this non-random distribution is probably the major cause of the delayed elastic effect. At higher temperatures the more rapid thermal creation and destruction of the defects around which flow took place again worked to give a more random distribution. Chilling from these higher temperatures failed to give permanent birefringence.

STRENGTH AND VISCOELASTIC MODEL OF SODA-LIME GLASS AT TEMPERATURES FROM 1000°F. to 1400°F., by Theodore C. Baker, Owens-Illinois Technical Center, Toledo, Ohio.

This work was stimulated by the fact that glass breaks more readily at higher temperatures than lower temperatures.

An apparatus was described that measured the strength and elongation of glass rods in times as low as 0.001 second and at temperatures from 1000°F. to 1400°F. From the data obtained it was possible to compute the viscoelastic model of a soda-lime glass. The average strength of the rods measured varied from 21,000 to 9800 lbs. /in.^{2} and appeared to be correlated with part of the viscoelastic model.

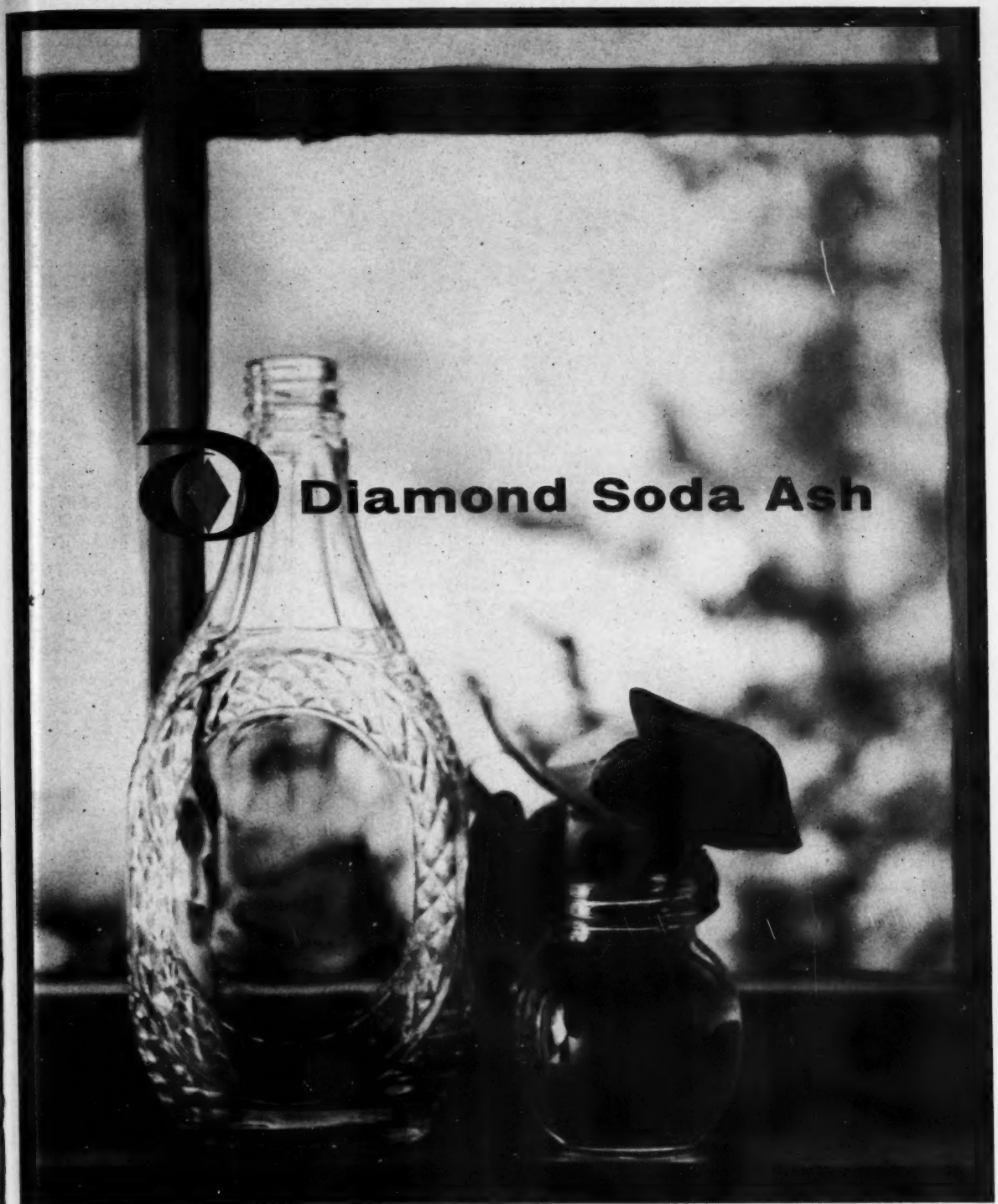
APPLICATION OF RHEOLOGY TO GLASS—A SUMMARY AND CRITIQUE, by Wladimir Philippoff, The Franklin Institute, Philadelphia, Penna.

Solid glass below 400°C. is nearly an ideal elastic solid whose mechanical behavior is fully described by the classical theory of elasticity. Molten glass above a temperature of 1000°C. behaves as an ideal viscous liquid. It is obvious that between these behaviors there must be a transition region where both properties occur. This is the range of application of rheology, or more specifically, the mechanics of viscoelastic bodies.

The occurrence of an elasticity and a viscosity introduced time-dependent properties that have been observed either in dynamic testing with harmonic loading, stress relaxation, or changing load as has been discussed in the preceding papers. Besides that, however, the elasticity caused by its nature an elastic response to loading which can be termed *recoverable shear*. This response led to new stress phenomena, for instance the *normal stresses*.

Best developed is the theory of linear viscoelasticity that has also been described in the preceding papers. However, in the use of glass in the particular temperature range mentioned, large deformations were usually applied for which linear-viscoelasticity by its nature was not applicable. Thus the theory of rubberlike elasticity that has been well developed may be applicable without resorting to the assumption of small strains. "Whether it can be applied or not depends exclusively on the amount of elastic deformation which to our knowledge has not yet been measured for glass."

(*Continued on page* 388)



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Diamond Chemicals

(*Continued from page* 386)

Wednesday Morning

The Wednesday morning session was presided over by Neill M. Brandt, Mellon Institute, Pittsburgh, Pennsylvania.

STRENGTH AND STATIC FATIGUE OF ABRADED GLASS UNDER CONTROLLED AMBIENT CONDITIONS—III. THE EFFECT OF VARIOUS ABRASIONS AND THE UNIVERSAL FATIGUE CURVE, by R. E. Mould, Preston Laboratories, Inc., Butler, Pennsylvania.

This report covered the results of part of an extensive study of the strength of glass. The test specimens were standard microscopic slides, and the static fatigue of wet glass under controlled ambient conditions was determined.

Static fatigue curves (strength vs. load duration) were obtained for specimens immersed in room temperature distilled water and in liquid nitrogen (77°K) after the specimens had been subjected to various abrasion treatments. The low temperature strength was independent of load duration, and for surface damage of simple geometry it was inversely proportional to the square root of the initial crack depth, consistent with the Griffith Theory. Abrasions of different geometry produced differing static fatigue curves at room temperature, and in one case curves actually crossed. If, however, the strength values for each abrasion are divided by the low-temperature strength for that abrasion and plotted against a reduced time coordinate, all the data could be fitted to a single *universal fatigue curve.* This analysis permitted a clear distinction between *linear* and *point* flaws consistent with the known geometry of the abrasions.

Linear flaws fatigue more rapidly than *point* flaws by a factor of 50, and for each type of damage the fatigue rate was inversely proportional to the exponential of the initial flaw depth. A detailed analysis of the data in terms of several static fatigue theories from the literature showed that none of them provided a complete and adequate explanation of the results.

The results have extreme practical application in that by a determination of the liquid nitrogen strength plus a knowledge of certain parameters and charts the characteristics of the flaws of unknown samples can be ascertained.

STRUCTURE OF GLASS AS SEEN FROM AN ATOMISTIC VIEWPOINT AND FROM A MOLECULAR VIEWPOINT, by Professor Herman Salmang, Maastricht, Netherlands.

Dr. Salmang is Professor of Glass Technology and Ceramics in the University of Aachen, Aachen, Germany. He was an invited speaker and emphasized the atomistic concept of the structure of glass, an approach different from that which had been heretofore discussed on the program.

An atomistic conception of glass structure is used in the crystal chemistry founded by G. M. Goldschmidt. A molecular conception is the foundation of G. Tammann's conception of glass as an undercooled fluid. The brilliant successes of crystal chemistry have led to an explanation of almost all properties of glass. Glass is seen then as a crystal with an overwhelming quantity of defect.

There still remain, however, many properties which are difficult to explain by crystal chemistry. Structural investigation, and the ability of drawing very thin threads and flowing very thin films, suggests that there are chains in glass not accounted for in the modern atomistic structure of Zacharaisen and Warren.

High viscosity finds still another explanation from a molecular viewpoint: SiO_2 as quartz and as a glass is a mixture of heteropolar and homopolar bonds. Homopolar bonds between various atoms give rise to dipole moments. This characteristic finds its expression in the piezoelectricity of quartz. Dipole moments of the molecule SiO_2 are the cause of viscosity, because the points of different electrical charge attract each other and augment viscosity just as does water, which is a fluid and not a gas as a result of the action of its dipole moments.

The presence of SiO_2– dipoles was suggested by Weyl as an interpretation of similar colors in aqueous solutions as in glassy solutions. There is another property of silica glass that cannot be explained by the atomistic viewpoint; it is the sudden change of density at −84°C. and at 1850°C. This change of density in the amorphous state can be compared to the change of density of water at +4°C. This change also cannot be explained without assuming a dipole nature of water. Tammann's ideas of molecules in glass are thus in no way absolute. They merit deeper discussion.

It was pointed out in the discussion that glass properties may best be interpreted on the basis of an ionic theory in some instances and on the basis of a molecular theory in others. There is danger, however, in oversimplication, and no single theory is adequate to explain all property behaviors.

TRANSFERENCE NUMBERS FOR WATER IN MOLTEN SODIUM SILICATES, by J. R. Hutchins, III, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Electromotive force measurements on a suitable concentration cell were used to determine the transference numbers for water in soda-silica glasses over a composition range from 17.1 to 45.1 weight per cent soda and up to water vapor partial pressures of 0.1965 atm. at 1250°C. The negative sign of the EMF generated by this cell indicated that throughout the composition range studied electrolytic migration or diffusion of water occurred predominantly through the transport of a positive ion, probably the proton. Extrapolation of the data to water vapor partial pressures of 1 atm. and comparison by the author with available data on electrical conductivity were used to discuss the role of water in the structure of these glasses.

Using a galvanic cell suggested by Wagner,

$$\underset{\text{air (p, air)}}{\text{Pt, A (pA)}} \quad \text{Glass Melt} \quad \text{Glass Melt} \quad \underset{\text{air (p, air)}}{\text{Pt, } H_2O \text{ (p}H_2O\text{)}}$$

where $pA = p\ H_2O$ and $p, air = p_{air}$.

The electromotive force was measured as a function of the water vapor partial pressure (0, 0.0725, 0.0942, 0.1215, 0.1550 and 0.1965) at the right hand electrode and was found to be proportional to the square root of the water vapor partial pressure; and, in all instances the EMF was negative. Calculations from the relations between these measured values and the transference number for water led to a relation of the type

$$t_n + = K\sqrt{pH_2O}$$

(*Continued on page* 390)

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(*Continued from page* 388)

which further justified the belief that water entered the structure of molten silicates as two statistically independent particles. The proportionality factor in the equation above varied from 0.108 to 0.333. The transference number – composition isobars showed that up to a soda content of approximately 30 per cent weight, the transference number is essentially constant. For higher soda content a rather sharp increase in the transference number was observed.

After suitable extrapolation of the EMF data to water vapor partial pressures of one atm., the corresponding transference numbers were compared to the results from the conductivity measurements made previously under these conditions. Employing the Nernst-Einstein relation, the author determined diffusion coefficients and ionic mobilities for the sodium and the hydrogen ions in wet and dry glasses. A comparison of these quantities for the sodium ion, wet and dry, indicated that for high-silica glasses, i. e. less than 28 weight per cent soda, the observed increase in electrical conductivity is wholly explained, within experimental limits of error, by water's increasing the number of conducting ions in the melt. The most probable structural equation for this composition range is

$$\equiv Si\text{-}O\text{-}Si\text{-} = + H_2O\ (g) = \equiv Si - OH + HO\text{-}Si \equiv$$

For glasses with higher soda content the presence of water decreased the conductivity. The mobility and the diffusion coefficient for the sodium ion in a wet glass were markedly less than corresponding values for the sodium ion in a dry glass, with the difference increasing with increasing soda content. Any structural explanations for these latter observations would be too speculative without additional data. The values for the mobilities at 1250°C. for the hydrogen and the sodium ions—wet and dry—were in the order of 10^{-3} to 10^{-4} cm. per sec. per volt per cm. respectively.

Diffusion coefficients for these ions at 1250°C. were in the order of 10^{-4} and 10^{-5} cm.^{2} per sec. respectively. The regular increase in the mobility and the diffusion coefficient of the hydrogen ion with increasing soda content is probably best explained by a gradual decrease in the potential barrier a hydrogen ion must overcome to enter the conducting mechanism.

Although transference numbers were measured at water vapor partial pressures of 0.0725 atm. at 1100 and 900°C., activation energies could not be calculated for the diffusion coefficients and the mobilities mentioned above, in view of the ambiguity of the temperature dependence of the transference number owing to the errors associated with these measurements.

Wednesday Afternoon

R. D. Maurer, Corning Glass Works, Corning N. Y., was chairman of the Wednesday afternoon session.

IMPROVED APPARATUS FOR RAPID MEASUREMENT OF THE VISCOSITY OF GLASS AT HIGH TEMPERATURES, by Ralph L. Tiede, Owens-Corning Fiberglas Corporation, Research Center, Newark, Ohio.

Apparatus was described for measuring the viscosity of glass in the range of 6.5 to 13,000 poises. The measurement was made with a commercial Brookfield viscom-

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eter, which utilized the familiar rotating cylinder method. The glass was melted in a platinum container which also served as the heating element. A special electrical circuit and control system made rapid heating and cooling of the element possible. This fact, combined with the intimate contact between the glass and the source of heat, plus the use of a relatively small glass sample (75 grams) resulted in rapid attainment of temperature equilibrium.

As a result, only about 15 minutes was required per point on the viscosity versus temperature curve, and up to 6 curves may be obtained in an 8-hour day. Primarily, because of good temperature control and the use of a device for accurately positioning the rotating spindle in the glass, precision was quite good. Repair was simple and maintenance low. The apparatus may be used for either research or control purposes.

Through the use of curves, if a scale reading is taken and if the rpm of the spindle is known, the log can be run. Six viscosities per day can be made, and results can be checked within 10° with data obtained by other means.

Determinations were made periodically with standard glass, and any changes or corrections were made in the apparatus. It is believed that if the viscosity differences in two glasses would be as little as 2°, it would be indicated on the instrument.

The results were compared with a Brookfield viscometer.

TEMPERING OF GLASS TUBES, by Oscar H. Grauer, Fischer and Porter Company, Hatboro, Pennsylvania.

The problem of tempering a flow-meter tube without changing its dimensions and calibration or hampering its use was a most difficult one. Because the geometry of the tube was most complicated, the problem presented many complexities. Because borosolicate glasses were used, the coefficient of expansion was only about one-third that of soda-lime glasses.

Numerous polariscopic patterns were made and studied and were most useful in showing the distribution of strain, but such patterns do not provide quantitative measurements. Inhomogeneities in the glass were also apparent. The strain distribution at the head of the tube was found to be highly important.

Tempering in air, oil, and solder were all tried. Increases in strength of about 100 per cent were noted in the oil-quenched tubes, and lesser strengths were provided in other media.

Different tempering schedules were attempted. Increases in the strength of tubes were assessed for short-term and long-term durations. Short-term (millisecond range) stresses were produced by hydraulic shock waves through a controlled "water hammer."

CRUSHING RESISTANCE OF GLASS RECEIVING-TUBE ENVELOPES IN A GAS PRESSURE CHAMBER, by John Gallup, Electron Tube Division, Radio Corporation of America, Harrison, New Jersey.

This paper described an investigation of the pressure at which a number of different types and sizes of receiving-type electron tubes failed. The criterion of failure was considered to be disappearance of the getter flash, although failure was normally so violent as to leave no doubt of its occurrence. Tubes ranging from the smallest subminiature to the largest receiving tube (type 6BG6-G)

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- ☐ 4. Whisker guards

Appearances to the contrary, No. 3 is the right answer. These are miniature diode cases made of glass tubing accurate to a few thousandths of an inch. The tubing is mass-produced in short lengths by a new method developed at Corning Glass Works. Throughout nearly 70 years as a supplier of Soda Ash to the glass industry, Wyandotte has watched glass keep pace with progress in many fields. Today, as in the past, Wyandotte is a working partner supplying technical assistance and raw-material chemicals to those great companies marking milestones in glass progress.

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were tested. The larger tubes withstood pressure up to 400 and 500 pounds per square inch, while the smaller ones did not fail until pressures of 1900 to 2000 pounds per square inch were attained. The influences of shape and type of basing were considered. The test equipment employed was a stainless steel, one-gallon autoclave pressured from cylinders of compressed nitrogen at room temperature.

Every effort was made to ascertain the cause and source of tube failures. In some instances the failure was traced to the Bakelite base, reentrant stems, seals, surface flaws, glass-to-metal seals, as well as residual strain. Defects were also found to vary somewhat depending upon the size of the bulbs and their variance in structure.

The glass usually failed to a powder although some failed with a cracking noise and without implosion. Fracture tests were also tried in water, but a fine glass powder was still produced and there was no evidence that the water cushioned the implosion.

This was a very practical paper, and the tests were instigated by a request for information related to the hydraulic pressures which glass-receiving tubes can be expected to withstand without cracking or imploding.

OBSERVATIONS OF THE PLASTIC DEFORMATION AND FRACTURE OF GLASS UNDER CONCENTRATED FORCES, by O. K. Salmassy, AVCO Manufacturing Corporation, Research and Advanced Development Division, Wilmington, Massachusetts.

This paper described observations made on the flow and fracture phenomena occurring in soda-lime-silica glass during the hardness indentation process. A technique for simultaneous observation and indentation was described. The effects of loading and unloading, and the effects of the magnitude of normal force applied upon the nature of the flow and fracture produced were also described. Plastic flow without fracture, of a magnitude beyond that heretofore observed in the indentation process, was reported. The concept was advanced that the stress state induced by concentrated forces may reduce the influence of an embritting flaw. Various concepts for explaining the plastic flow in glass under concentrated forces were discussed.

The various types of fractures produced were illustrated and were shown to contain radial cracks and chips. Profiles of the surface were also helpful in identifying the fractures. The data indicated that the Ainsworth concept appears to be valid and true.

MELTING AND REFINING OF A SODA-LIME-SILICA GLASS AND THE EFFECT OF REFINING AGENTS, by Michael Cable, University of Sheffield, England.

This paper was divided into three parts: a report on the refining behavior of soda-lime-silica glass, theoretical discussion of the results, and experimentation that provided useful information concerning the mechanism of refining.

Melts of 73.5 SiO_2, 16.5 Na_2O and 10.0 CaO (weight per cent) were found in an electric furnace at 1400 and 1450°C. Specimens were cast from the melts at various founding times, and measurements were made of the number, size, and size distribution of the seed. Suitable additions of refining agents decreased the seediness at the batch-free time, which was shortened, and, in addition, accelerated refining.

A theoretical approach showed that the exponential relation between the number of seed of one size and time could not be caused by the rise of bubbles through the melt; also, small seed disappeared more rapidly than expected. An approximate solution of the diffusion problem allowed the behavior of bubbles in a liquid to be predicted when gas diffused into or out of them. This led to the hypothesis that bubbles are removed by dissolving in the glass. There is some evidence to support this hypothesis in the results of other workers.

Experiments to indicate the oxygen saturations of the melts supported the view that the function of oxygen was to diffuse out of bubbles allowing them to dissolve more quickly; the function of arsenic during refining was to absorb oxygen. Fining behavior was thus enhanced by the formation of oxygen-rich bubbles.

It was concluded that two processes were important in refining the rise of large bubbles through the melt and the dissolving of small ones. An essential part of the refining action of arsenic occurred during melting; therefore, melting and refining could not be considered as two independent processes. Refining was much influenced by the gases present in the seed and dissolved in the glass.

This paper was another practical one designed to improve the melting and fining techniques of glass melting.

Business Meeting

At the business meeting of the Glass Division, the standing committee reports were presented, and a rough draft of the Manual Committee's Report was presented by Mr. Michener. This manual was presented in preliminary form so that it might be a guide for the incoming officers. This extensive piece of work is appreciated by all members.

Division Officers

The Division officers for the coming year are as follows:

EXECUTIVE COMMITTEE

Frank R. Bacon, CHAIRMAN, Owens-Illinois Technical Center, Toledo 1, Ohio.
Guy E. Rindone, VICE CHAIRMAN, Department of Ceramic Technology, Pennsylvania State University, University Park, Pennsylvania.
Fay V. Tooley, SECRETARY, University of Illinois, 611 W. Oregon, Urbana, Illinois.
August C. Siefert, TRUSTEE, Owens-Corning Fiberglas Corporation, Newark, Ohio.
Neill M. Brandt, CONSULTANT and PAST CHAIRMAN, Mellon Institute, 4400 Fifth Avenue, Pittsburgh 13, Pennsylvania.

PAPERS AND PROGRAMS COMMITTEE

Robert D. Maurer, CHAIRMAN (Term '57-'60), Corning Glass Works, Corning, New York.
Clarence L. Babcock, Owens-Illinois Technical Center, Toledo 1, Ohio (Term '58-'60).
Harold E. Simpson, State University of New York, College of Ceramics at Alfred University, Alfred, New York, (Term '59-'62).

Fall Meeting

The Fall Glass Meeting will be held at Galen Hall, Wernersville, Pennsylvania, October 15-16. The program planned for this meeting is a *Symposium of Radiation Effects*, under Chairman Norbert S. Kreidl of Bausch and Lomb Optical Company and a workshop on *Strength of Glass*, with Neill M. Brandt, Mellon Institute, Pittsburgh, Penna., as Chairman. Mrs. Charles Gum will be chairman of the Ladies Committee and Mr. Charles Gum will be chairman of the Golf Committee.

Lead Sulphide Films

(*Continued from page* 361)

is now washed. This process is carried out with running water to free it from any reacting or contaminating compounds resulting from the reaction during the process of film formation.

Drying

The film is then dried by any of the conventional methods, such as by standing the glass plate up at an angle, allowing the moisture to drain off. This may be accelerated by subjecting the film to an increase in temperature sufficiently high to aid evaporation.

Lacquering

The film, when perfectly dry, is lacquered in order to prevent scratching or defacing. This step is similar to that used in silvering in that any good shellac compound may be applied with a brush (manual) or by air gun.

Discussion of Techniques

Lead Tartrate Method

Reynolds, subsequently with the aid of Dr. Grubb, developed two formulations.

1)	Thiourea	15 grams
	Water	1 liter
2)	Lead tartrate	75 grams
	Sodium hydroxide	40 grams
	Water	1 liter

Increasing the proportions of solutions 1 and 2 will give rise to translucent or opaque films respectively, of lead sulphide on the given surface.

Lead Acetate Method

In the Kutscher report, reference is made to Holdt's technique consisting of:

1)	Lead acetate	379.2 grams

(Dissolved in water containing 1.0 cc. concentrated acetic acid and diluted to a total volume of 1 liter.)

2)	Thiourea	76.12 grams
	Water	1000 cc.
3)	Sodium hydroxide	400 grams
	Water	1000 cc.

To obtain the initial sulphide film, take:

Solution 1	0.5 cc.
Solution 2	1.0 cc.

To which is added:

Water	38.5 cc.

This is heated to 35° C. (95° F.), subsequently adding:

Solution 3	0.75 cc.
Water	29.25 cc.

Mix the combined solutions for 1½ minutes and pour onto the sensitized surface. In about six or seven minutes, the lead sulphide film will begin to form, and in about 30 minutes the film is complete. The glass is washed with running water and a second coat is applied.

Colbert and Morgan formed optical light filters by using thiourea and lead acetate solutions in an acid

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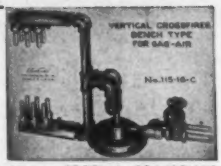

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media, consisting of:

1) Sodium hydroxide	3.18 per cent
Rochelle salts	0.00054 "
2) Lead acetate	3.7 per cent
Acetic acid	0.264 "
3) Thiourea	2.64 per cent

These solutions are mixed together in equal proportions just prior to being poured onto the glass surface. It takes about 8½ minutes to form the lead sulphide film.

The recommended temperature of the glass is 68° C.

A modified formulation accredited to these inventors consists of:

1) Sodium hydroxide	1.06 per cent
2) Lead acetate	1.23 per cent
3) Thiourea	0.88 per cent
Acetic acid	0.088 "
Rochelle salts	0.00018 "

Equal volumes are used of each of the solutions.

A modified formulation, according to these inventors, is made up of:

1) Lead acetate	1 part*
Sodium hydroxide	1½ parts
Water	24 "
2) Thiourea	2 parts
Alcohol	10-30 "
Water	96 "

* All parts are by weight.

In the cold process, the difference is in the proportions of the foregoing compounds (solutions), and is made up of 1 part of solution *2* to 1 part of solution *1*. These are mixed and allowed to stand for about 15 minutes, after which 1 part of solution *3* is added, and at once poured onto the given surface since this solution will deposit the lead sulphide very rapidly.

An Anonymous[00] writer, through the Office of the Technical Services, Department of Commerce, states that a "black mirror" can be made from the following formulation:

1) Thiourea	10 grams
Water	1 liter
2) Lead acetate	40 grams
Water	1 liter
3) Sodium hydroxide	20.2 grams
Water	1 liter

The proportions of the three solutions are:

Solution 1	100 cc.
Solution 2	25 cc.
Solution 3	50 cc.

These solutions should be kept at 40° C. and maintained at that temperature for a period of 15 minutes until the "black mirror" has been formed.

Pessel, in order to facilitate the adherence of lead sulphide films onto sheets of ethylcellulose plastics, first coats them with a film cyclized rubber or polystyrene dissolved in toluol. After the solvent (toluol) has evaporated, the lead sulphide solution is made up of:

1) Thiourea, 2 per cent solution	50 cc.
2) Sodium hydroxide, 10 per cent solution	25 cc.
3) Lead acetate, 10 per cent solution	25 cc.

The solutions are heated to 140° F. and mixed.

Colbert and Colbert used:

1) Lead acetate	1 ounce
Water	24 ounces
2) Sodium hydoxide	2 ounces
Water	32 ounces
3) Thiourea	1 ounce
Water	48 ounces

The recommended temperature is 95° F. and the proportions between the three solutions are:

Solution 1	4 parts
Solution 2	1 part
Solution 3	2 parts

The first formulation accredited to Colbert and Colbert using lead acetate consists of:

1) Lead acetate	1 ounce
Water	24 ounces
2) Sodium hydroxide	2 ounces
Water	32 ounces
3) Thiourea	1 ounce
Water	48 ounces

Solutions *1* and *3* are mixed in the proportions of 4 parts solution *3* to 1 part of solution *1*. Thereafter 1 part solution *2* is added to 5 parts of the combined solutions *1* and *3*. The recommended temperature is in the neighborhood of 95° F.

A slight modification of the foregoing formulation is made up of:

1) Lead acetate	0.5 gram
Water	12 ounces
2) Sodium hydroxide	21 grams
Water	12 ounces
3) Thiourea	28 grams
Water	12 ounces

The temperature recommended is 95° F.

Bruckman adds salts of tin, antimony or arsenic (which he terms "compounds") to lead acetate film-forming compounds, in this formulation:

1) Sodium hydroxide, 2 per cent solution	3 parts
2) "Compound"	4 parts
3) Lead acetate, 2 per cent solution	1 part
4) Thiourea, 2 per cent solution	3 parts

Solutions *1* and *2* are mixed; subsequently solutions *3* and *4* are added.

Eckerlin, to form his version of etching surface, used:

1) Thiourea	1 part
Water	50 parts
2) Lead acetate (diluted solution)	50 parts
Potassium hydroxide (diluted solution)	50 parts

Hansell has described in detail formulations for obtaining lead sulphide photo-conduction cells for use as infra-red-sensitive, or secretive, communication purposes by Allgemeine Eletrizate Gesselschaft in Germany during World War II. The lead sulphide films are made from the following solutions:

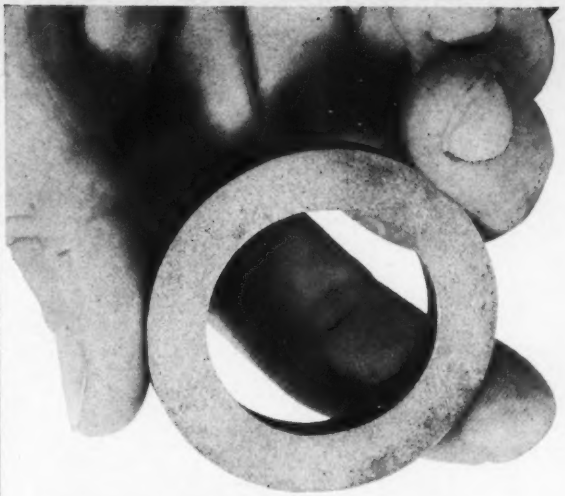
1) Lead acetate	0.05 mol/liter
2) Sodium hydroxide	0.5 mol/liter
3) Thiourea	0.5 mol/liter

To precipitate the lead sulphide film, the three solutions at 20° to 25° C. are mixed, aged for 20 seconds, and poured onto the surface to be coated, consisting of platinum-gold electrodes in the form of a grid. After a coating of the desired thickness is formed, it is aged for several hours at a temperature not exceeding 100° C.

The cell so formed is now mounted in a glass bulb and evacuated. Such a surface has a maximum response in wave lengths of 2 to 3 microns and the limit of response of about 3.5 microns. A modified formation accredited to "AEG" is made up of:

1) Lead acetate	0.019 mol/liter
2) Potassium hydroxide	0.19 mol/liter
3) Thiourea	0.10 mol/liter

These solutions are mixed at 25° C. and then placed in contact with the mounting surface to precipitate the lead sulphide film. It is claimed that when the film is



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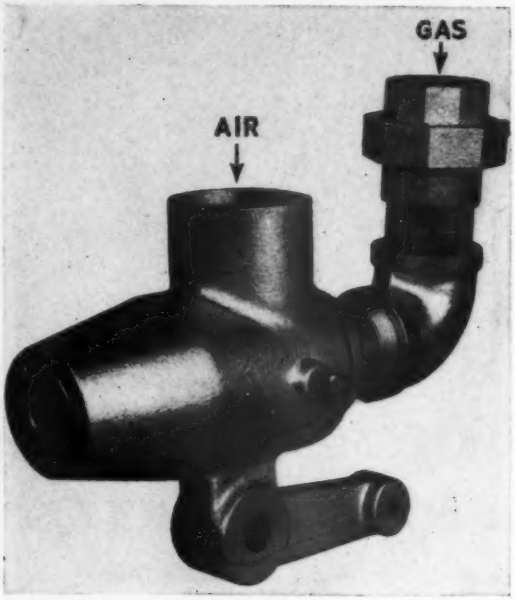

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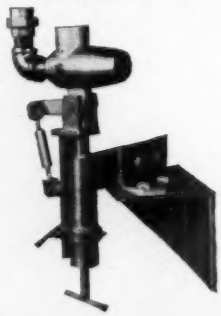

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first formed, it is not light-sensitive, but is made light sensitive by oxidation in air at 32.5° C. During this oxidation, the film is observed to change from yellow, to violet, to dark blue and then to light blue. Oxidation is stopped at this point.

The time required for oxidation varies greatly according to the age of the film and its previous history. A freshly prepared film requires from 10 to 30 minutes for the oxidation process, whereas one which has been held at 160° C. for eight days requires only about 1.5 minutes. After the oxidation process, the cell changes slowly in characteristics for about eight days.

Another interesting difference between the two processes, is that the "AEG" cell makes use of "Aquadag" (colloidal graphite) electrodes, instead of platinum-gold grid electrodes previously referred to. Cells made according to the present technique have a peak sensitivity at wave-lengths between 0.5 and 1.0 micron.

Hansell likewise reported the "Elec" photo-cell which consists of:

1) Lead acetate	400 grams
Water	1000 cc.
2) Thiourea	40 grams
Water	340 cc.
3) Sodium hydroxide	240 grams
Water	360 cc.

The three solutions are mixed in about the order of 3:1:1. Authorities differ on the exact ratios which should be used for best results, perhaps due to variations in the age, physical or chemical condition, and purity of the solutions.

Gardner and Case of the National Bureau of Standards suggested the following formulation:

1) Thiourea	1 gram
Water	50-75 cc.
2) Lead acetate	50-75 cc.
(dilute solution)	
Ammonia	25 cc
(dilute solution)	

Equal volumes of solutions 1 and 2 are used.

For his rectifier elements, Henderson recommends the formation of the three solutions consisting of:

1) Lead acetate	3.2 grams
Water	1 liter
2) Thiourea	10 grams
Water	1 liter
3) Sodium hydroxide	6.1 grams
Water	1 liter

Equal volumes of each of the three solutions are mixed together and poured onto the glass surface.

Heidenhain makes a two per cent solution of each of the three compounds and combines equal portions of each solution to form the lead sulphide films on glass.

Anderson uses the following solutions for forming his type of photo-cell:

1) Sodium hydroxide	0.5 N
2) Thiourea	0.5 N
3) Lead acetate	0.05 N

Mix equal parts of the three solutions and pour onto the glass surface.

Sodium Hyposulphite.

Beutel and Kutzelnigg deposit lead sulphide films on metal discs by electrolysis, using sodium hyposulphite.

(To Be Concluded)

Research Digest
(*Continued from page* 376)

tion is continuous. This indicates that no 'compounds' in the usual meaning of the word exist in the molten state. This conclusion coupled with the linear variation of properties with respect to temperature and composition implies a continuous variation of structure as these parameters are altered, and indicates that any picture of the structure of a particular composition at a certain temperature will only be the statistical average state of the system. Coupled with this broad picture, the most striking property of the system is the increase in surface tension with temperature. Anomalous behaviour of this type has been observed by other workers and various possible mechanisms for such behaviour have been discussed by King. Of these mechanisms, association seems the most acceptable. While not easily applicable in the case of simple liquids it is more readily applied to silicate liquids.

Solid silicates are characterized by the arrangement of four oxygen atoms around a silicon atom at the corners of a nearly regular tetrahedron. The complexity of these materials arises from the variety of ways in which these basic groups can be joined together. The structures range from a three-dimensional network to simple SiO_4^{4-} anions.

In the liquid state the long-range order of the crystalline state is destroyed and though ordered arrangement exists on a short-range basis the whole mass exhibits a random orientation.

As the silica network is broken down the number of separate 'molecules' will increase and it is on the number of these that the surface tension will depend, as in the case of associated liquids it depends on the relative proportions of associated and dissociated molecules present.

In the lime-alumina-silica system additions of lime gradually break down the large molecules until complete breakdown into the simple SiO_4^{4-} groups has occurred. Additions of alumina can produce similar breakdown but since aluminium can also enter the silica network-forming AlO_4^{5-} the breakdown would be expected to be less. Thus the surface tension would be highest for compositions high in lime, somewhat less for compositions where some of the lime is replaced by alumina and less still if replacement is by silica.

Increases in temperature should have an additional disruptive effect. The results indicate that in general this is greater where the previous degree of disruption is least, i.e. for compositions high in silica. The slight increase in temperature coefficient with increasing alumina may be due to the tendency to form anions but precise effects are difficult to predict because the proportion of aluminium in the network is unknown.

The overall picture of the structure of molten silicates which emerges is of a dynamic equilibrium between the various possible silicate groupings. This equilibrium is altered, in a way which is predictable in general terms, by changes in composition and temperature, and this change is reflected in the physical properties. The values of surface tension and density and their temperature coefficients, which result from the experimental study, confirm the model postulated on the basis of the conception of molten silicates as associated liquids.

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